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TITLE**PROCESSES FOR PURIFYING PERFLUOROCYCLOBUTANE**5 **CROSS REFERENCE TO RELATED APPLICATIONS**

This application claims the priority benefit of U.S. Provisional Application 60/076923, filed March 5, 1998.

FIELD OF THE INVENTION

10 The present invention relates to azeotropic and azeotrope-like compositions containing perfluorocyclobutane, and azeotropic and extractive distillation processes for separating perfluorocyclobutane from a first mixture comprising perfluorocyclobutane and halogenated impurities, such that perfluorocyclobutane of high purity is obtained in a high-recovery efficiency.

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BACKGROUND OF THE INVENTION

Gaseous fluorine-containing compounds are used by the electronics industry in processes to manufacture semiconductor devices. The major use of perfluorocyclobutane (PFC-C318) is in plasma etching silicon-type materials during semiconductor device fabrication. Plasma etchants such as PFC-C318 fragment under the plasma conditions, and these fragmentation products interact with the surface of the semiconductor device, modifying it so as to lay down the electrical pathways and providing for the surface functionalities that define an integrated surface.

25 Chemicals such as PFC-C318 used as plasma etchants in semiconductor manufacturing applications are generally referred to as "electronic gases". Electronic gases having high purity are critical in this application. It is known that even very small amounts of impurities in electronic gases can result in wide line width and thus less information per semiconductor device when such impure gases are used in semiconductor device manufacturing tools. Moreover, the presence of these impurities, including particulates, metals, moisture, and halocarbon impurities, even when present only in the parts-per-million level, increases the defect rate in the production of high-density integrated circuits. As a result, there is an increasing demand by the electronics industry for very high purity etchant gases, and an increasing market value for the materials having the required purity. Identification of impurities and methods for their removal represent a significant aspect of preparing the etchant gases for these applications.

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PFC-C318, in its pure state, exhibits properties that are valued for integrated circuit manufacturing and may be used in a variety of manufacturing steps. The desire for greater precision and consistency of the effect electronic gases such as PFC-C318 have during integrated circuit manufacture has made
5 extremely high-purity gases critical in such applications. The presence of halogenated impurities in the PFC-C318 is objectionable for the intended uses in this field. Processes that would allow for manufacture of PFC-C318 having a purity that approaches 99.999 molar percent purity are desirable, and processes that would provide at least 99.9999 molar percent purity PFC-C318 for electronic
10 gas applications would be preferred.

PFC-C318 may be produced by the pyrolysis of chlorodifluoromethane (CHClF_2 , HCFC-22), as is disclosed in US Patent No. 5,129,997. It is difficult to obtain a PFC-C318 product having very high purity from the product stream produced by this process because a variety of halogenated
15 impurities are also produced that are extremely close-boiling to PFC-C318 in their separated and pure states or otherwise exhibit non-ideal behavior such that their relative volatilities compared to PFC-C318 approaches or even becomes 1.0. Impurities whose relative volatilities approach or equal 1.0 compared to PFC-C318 make their separation from PFC-C318 by conventional distillation
20 ineffective in recovering a PFC-C318 product from which impurities have been removed. Such separation is particularly problematic where it is desired that the recovered PFC-C318 product be substantially-free of halogenated impurities and where the PFC-C318 product needs to be recovered from a mixture comprising PFC-C318 and impurities with high-recovery efficiency.

25 Conventional methods for producing a PFC-C318 product are not capable of producing a PFC-C318 product having a 99.999 or greater molar percent purity due to their inability to remove a variety of the halogenated impurities from the PFC-C318 product. The production of PFC-C318 having 99.999 or higher molar percent purity was not known before the present invention.

30 Wiist in GB 886,714 discloses an extractive distillation process using aromatic or chlorinated aromatic hydrocarbons as extractive agents for separating a mixture of perfluoropropylene and perfluorocyclobutane from other halogenated compounds obtained upon the pyrolysis of chlorodifluoromethane.

The present invention solves problems associated with conventional
35 distillation methods by providing distillation processes for removing halogenated impurities from PFC-C318 so as to produce highly-purified PFC-C318 with high-recovery efficiency.

SUMMARY OF THE INVENTION

The present invention comprises PFC-C318 substantially free of
halogenated impurities, preferably containing less than 10 parts-per-million-molar
5 of halogenated impurities.

The present invention further comprises azeotropic compositions consisting essentially of: perfluorocyclobutane (PFC-C318) and 2-chloro-1,1,1,2-tetrafluoroethane (HCFC-124); perfluorocyclobutane (PFC-C318) and 1,1,2,2-tetrafluoroethane (HFC-134); perfluorocyclobutane (PFC-C318) and 1,1,1,2-tetrafluoroethane (HFC-134a); and perfluorocyclobutane (PFC-C318) and 1,1-difluoroethane (HFC-152a). The present invention further comprises azeotropic and extractive distillation processes for separating perfluorocyclobutane (PFC-C318) from a first mixture comprising perfluorocyclobutane (PFC-C318) and halogenated impurities.

According to one aspect of the present invention, there is provided a process for separating perfluorocyclobutane (PFC-C318) from halogenated impurity, comprising:

distilling a mixture of perfluorocyclobutane (PFC-C318) and halogenated impurity in the presence of an entraining agent selected from the group consisting of ethers, ketones, alcohols, saturated hydrocarbons and saturated hydrochlorocarbons, and

recovering perfluorocyclobutane (PFC-C318) containing less than 10 parts-per-million-molar of halogenated impurity.

According to another aspect of the present invention, there is provided a process for separating perfluorocyclobutane (PFC-C318) from a first mixture of perfluorocyclobutane (PFC-C318) and halogenated impurity selected from the group consisting of 1,1,2,2-tetrafluoroethane (HFC-134), 1,1,1,2-tetrafluoroethane (HFC-134a) or 1,1-difluoroethane (HFC-152a), wherein the amount of perfluorocyclobutane (PFC-C318) in the first mixture is in excess of the amount of perfluorocyclobutane (PFC-C318) in an azeotropic or azeotrope-like composition of perfluorocyclobutane (PFC-C318) and halogenated impurity, comprising:

a.) distilling the first mixture to form an azeotropic or azeotrope-like composition of perfluorocyclobutane (PFC-C318) and halogenated impurity as a second mixture, wherein said azeotropic or azeotrope-like composition is selected from the group consisting of:

i.) an azeotropic or azeotrope-like composition consisting essentially of from 24.6 to 23.2 mole percent of perfluorocyclobutane (PFC-C318) and from 75.4 to 76.8 mole percent of 1,1,2,2-tetrafluoroethane (HFC-134), said composition having a boiling point of from -30°C at 10 psia to 80°C at 326 psia,

ii.) an azeotropic or azeotrope-like composition consisting essentially of from 9.9 to 0.6 mole percent of perfluorocyclobutane (PFC-C318) and from 90.1 to 99.4 mole percent of 1,1,1,2-tetrafluoroethane (HFC-134a), said composition having a boiling point of from -30°C at 12 psia to 40°C at 147 psia, or

iii.) an azeotropic or azeotrope-like composition consisting essentially of from 23.1 to 21.3 mole percent of perfluorocyclobutane (PFC-C318) and from 76.9 to 78.7 mole percent of 1,1-difluoroethane (HFC-152a), said composition having a boiling point of from -20°C at 19 psia to 80°C at 349 psia, and

b.) recovering said azeotropic or azeotrope-like composition as a distillation column overhead stream and perfluorocyclobutane (PFC-C318) as a distillation column bottom stream.

According to yet another aspect of the present invention, there is provided a process for separating perfluorocyclobutane (PFC-C318) from a first mixture of perfluorocyclobutane (PFC-C318) and halogenated impurity selected from the group consisting of 1,1,2,2-tetrafluoroethane (HFC-134), 1,1,1,2-tetrafluoroethane (HFC-134a) or 1,1-difluoroethane (HFC-152a), wherein the amount of halogenated impurity in the first mixture is in excess of the amount of halogenated impurity in an azeotropic or azeotrope-like composition of perfluorocyclobutane (PFC-C318) and halogenated impurity, comprising:

a.) distilling the first mixture to form an azeotropic or azeotrope-like composition of perfluorocyclobutane (PFC-C318) and halogenated impurity as a second mixture, wherein said azeotropic or azeotrope-like composition is selected from the group consisting of:

i.) an azeotropic or azeotrope-like composition consisting essentially of from 24.6 to 23.2 mole percent of perfluorocyclobutane (PFC-C318) and from 75.4 to 76.8 mole percent of 1,1,2,2-tetrafluoroethane (HFC-134), said composition having a boiling point of from -30°C at 10 psia to 80°C at 326 psia,

ii.) an azeotropic or azeotrope-like composition consisting essentially of from 9.9 to 0.6 mole percent of perfluorocyclobutane (PFC-C318) and from 90.1 to 99.4 mole percent of 1,1,1,2-tetrafluoroethane (HFC-134a), said composition having a boiling point of from -30°C at 12 psia to 40°C at 147 psia, or

iii.) an azeotropic or azeotrope-like composition consisting essentially of from 23.1 to 21.3 mole percent of perfluorocyclobutane (PFC-C318) and from 76.9 to 78.7 mole percent of 1,1-difluoroethane (HFC-152a), said composition having a boiling point of from -20°C at 19 psia to 80°C at 349 psia, and

b.) recovering said azeotropic or azeotrope-like composition as a distillation column overhead stream and halogenated impurity as a distillation column bottom stream.

BRIEF DESCRIPTION OF THE DRAWINGS

Fig 1 is a schematic diagram of a distillation system that can be used for practicing an aspect of the present process.

Fig 2 is a graphical representation of an azeotropic and azeotrope-like composition consisting essentially of PFC-C318 and HCFC-124 at a temperature of 20°C.

Fig 3 is a graphical representation of an azeotropic and azeotrope-like composition consisting essentially of PFC-C318 and HCFC-124a at a temperature of 20°C.

Fig 4 is a graphical representation of an azeotropic and azeotrope-like composition consisting essentially of PFC-C318 and HFC-134 at a temperature of 0°C.

Fig 5 is a graphical representation of an azeotropic and azeotrope-like composition consisting essentially of PFC-C318 and HFC-134a at a temperature of 0°C.

Fig 6 is a graphical representation of an azeotropic and azeotrope-like composition consisting essentially of PFC-C318 and HFC-152a at a temperature of 0°C.

DETAILED DESCRIPTION

The present invention includes PFC-C318 that is substantially-free of impurities. By impurities is meant any halogenated compounds other than PFC-C318. By substantially-free or substantially-pure is meant that the PFC-C318 produced by a process of the present invention contains less than 10 parts-per-million-molar (ppmm), preferably less than 1 ppmm, and most preferably less than 100 parts-per-billion-molar (ppbm), of halogenated impurity. Thus, included in the present invention is PFC-C318 having less than 10 ppmm, preferably less than 1 ppmm, and more preferably less than 100 ppbm, of impurities. Analytical methods that may be used to analyze such concentrations of impurities in a PFC-

C318 product are disclosed in "Examining Purification and Certification Strategies for High-Purity C₂F₆ Process Gas", Micro Magazine, April 1998, beginning page 35, hereby incorporated by reference.

Processes used to produce PFC-C318 may simultaneously produce a variety of halogenated impurities in the PFC-C318 product stream. Examples of halogenated impurities that may be found in a PFC-C318 production stream include linear and cyclic, saturated and unsaturated, perfluorocarbons (PFCs), chlorofluorocarbons (CFCs), hydrochlorofluorocarbons (HCFCs), hydrofluorocarbons (HFCs), and hydrochlorocarbons (HCCs). Representative examples from these classes of halogenated impurities include: PFC-31-10 (normal or iso-C₄F₁₀, perfluorobutane isomers), PFC-41-12 (C₅F₁₂, perfluoropentane isomers), PFC-1318my (cis and trans-CF₃CF=CFCF₃), PFC-1318c (CF₃CF₂CF=CF₂), PFC-1216 (HFP or CF₃CF=CF₂), PFC-1114 (TFE or CF₂=CF₂) perfluoroisobutene (CF₂=C(CF₃)₂), CFC-114 (CF₂ClCF₂Cl), CFC-114a (CFC1₂CF₃), CFC-216ba (CF₃CFC1CF₂Cl), CFC-217ba (CF₃CC1FCF₃), CFC-1113 (CC1F=CF₂), HCFC-22 (CHClF₂), HCFC-21 (CHCl₂F), HCFC-124 (CHFClCF₃), HCFC-124a (CC1F₂CHF₂), HFC-134 (CHF₂CHF₂), HFC-134a (CH₂FCF₃), HFC-152a (CH₃CF₂H), HFC-125 (CF₃CF₂H), HFC-227ca (CF₃CF₂CHF₂), HFC-227ea (CF₃CHF₂CF₃), HFC-1225zc (CF₃CH=CF₂), HFC-236ca (CHF₂CF₂CHF₂), HFC-236ea (CHF₂CHF₂CF₃), HFC-236fa (CF₃CH₂CF₃), HCC-30 (CH₂Cl₂), HCC-40 (CH₃Cl), and HCC-160 (CH₃CH₂Cl).

Several of these impurities form azeotropic or azeotrope-like mixtures with PFC-C318, making high-recovery efficiency of substantially-pure PFC-C318 from such product streams difficult. Such impurities that form azeotropic or azeotrope-like mixtures with PFC-C318 include each of HCFC-124, HCFC-124a, HFC-134, HFC-134a and HFC-152a. Other halogenated impurities produced during the pyrolysis of HCFC-22 that represent a significant problem in obtaining a substantially-pure PFC-C318 product include PFC-1318my, PFC-31-10, PFC-1318c, CFC-114, and CFC-114a.

By high-recovery efficiency is meant that greater than 90%, preferably greater than 95%, of the PFC-C318 in a first mixture is recovered as a result of a purification process as a PFC-C318 product substantially-free of at least one halogenated impurity.

By azeotropic or an azeotrope composition is meant a constant-boiling mixture of two or more compounds that behaves as a pure compound. One way to characterize an azeotropic composition is that the vapor produced by partial evaporation or distillation of the liquid has the same composition as the liquid from which it is evaporated or distilled; i.e., the mixture distills/refluxes

without compositional change. Constant-boiling compositions are characterized as azeotropic when they exhibit either a maximum or minimum boiling point, as compared with that of a non-azeotropic mixture of the same components.

Azeotropic compositions are also characterized by a minimum or a maximum in the mixture vapor pressure relative to the vapor pressure of the neat components at a constant temperature.

By azeotrope-like is meant a composition that has a constant boiling characteristic or a tendency not to fractionate upon boiling or evaporation.

Therefore, the composition of the vapor formed is the same as, or substantially the same as, the original liquid composition. During boiling or evaporation, the liquid composition, if it changes at all, changes only to a minimal or negligible extent.

An azeotrope-like composition can also be characterized by the area that is adjacent to the maximum or minimum vapor pressure in a plot of composition vapor pressure at a given temperature as a function of mole fraction of components in the composition. A composition is azeotrope-like if, after about 50 weight percent of an original composition is evaporated or boiled off to produce a remaining composition, the change between the original composition and the remaining composition is no more than about 6 weight% and typically no more than about 3 weight% relative to the original composition.

By low-boiling-azeotropic or azeotrope composition is meant a composition that boils at a lower temperature at any given pressure than any one of the compounds that comprise it would separately boil at that pressure.

Alternately, by low-boiling azeotropic or azeotrope composition is meant a composition that has a higher vapor pressure at any given temperature than the vapor pressure of any one of the compounds that comprise the azeotrope would separately have at that temperature.

By high-boiling azeotrope is meant that an azeotropic or azeotrope-like composition boils at a higher temperature at any given pressure than any one of the compounds that comprise it would separately boil at that pressure.

Alternately, by high-boiling azeotrope is meant any azeotropic or azeotrope-like composition that has a lower vapor pressure at any given temperature than any one of the compounds that comprise it would separately have at that temperature.

It is possible to characterize an azeotropic or azeotrope-like composition as a substantially constant-boiling mixture that may appear under many guises, depending upon the conditions chosen, by several criteria:

* The composition can be defined as an azeotrope of two compounds because the term "azeotrope" is at once both definitive and limitative, and requires effective amounts of those two or more compounds for this

unique composition of matter which can be a constant-boiling composition.

5 * It is well known by those skilled in the art, that, at different pressures, the composition of a given azeotrope or azeotrope-like composition will vary at least to some degree, as will the boiling point temperature. Thus, an azeotropic or azeotrope-like composition of two compounds represents a unique type of relationship but with a variable composition that depends on temperature and/or pressure. Therefore, compositional ranges, rather than fixed compositions, are often used to
10 define azeotropes and azeotrope-like compositions.

 * An azeotrope or azeotrope-like composition of two compounds can be characterized by defining compositions characterized by a boiling point at a given pressure, thus giving identifying characteristics without unduly limiting the scope of the invention by a specific numerical composition,
15 which is limited by and is only accurate as the analytical equipment available.

 It is recognized in the art that both the boiling point and the amount of each component of the azeotropic composition may change when the azeotrope liquid composition is subjected to boiling at different pressures. Thus, an
20 azeotropic composition may be defined in terms of the unique relationship that exists among components or in terms of the exact amounts of each component of the composition characterized by a fixed boiling point at a specific pressure.

 It is recognized in this field that when the relative volatility of a system, for example, a mixture comprising PFC-C318 and a halogenated impurity
25 of the present invention, approaches 1.0, such defines the system as forming an azeotrope-like composition. Should the relative volatility be equal to 1.0, such defines the system as forming an azeotropic composition. Impurities whose relative volatility to PFC-C318 approaches or equals 1.0 are extremely difficult or impossible to separate from PFC-C318 by conventional distillation. By
30 conventional distillation is meant that the relative volatilities only of the components of the mixture to be separated are used to separate the components.

 To determine the relative volatility of any two compounds, a method known as the PTx method may be used. In this procedure, the total absolute pressure in a cell of known volume is measured at a constant temperature for
35 various compositions of the two compounds. Use of the PTx Method is described in detail in "Phase Equilibrium in Process Design", Wiley-Interscience Publisher, 1970, written by Harold R. Null, on pages 124 to 126; hereby incorporated by reference.

These measurements can be converted into equilibrium vapor and liquid compositions in the PTx cell by using an activity coefficient equation model, such as the Non-Random, Two-Liquid (NRTL) equation, to represent liquid phase nonidealities. Use of an activity coefficient equation, such as the NRTL equation is described in detail in "The Properties of Gases and Liquids," 4th edition, published McGraw Hill, written by Reid, Prausnitz and Poling, on pages 241 to 387, and in "Phase Equilibria in Chemical Engineering," published by Butterworth Publishers, 1985, written by Stanley M. Walas, pages 165 to 244. Both aforementioned references are hereby incorporated by reference.

Without wishing to be bound by any theory or explanation, it is believed that the NRTL equation, together with the PTx cell data, can sufficiently predict the relative volatilities of PFC-C318, halogenated impurities, and entraining agents of the present invention and can therefore predict the behavior of these mixtures in multi-stage separation equipment such as distillation columns.

Surprisingly, PFC-C318 and HCFC-124 have been found by the present inventors to form an azeotropic composition comprising 26.8 mole% PFC-C318 and 73.2 mole% HCFC-124 at 20°C and 49 psia (pounds-per-square-inch-absolute). From these data it has been calculated that PFC-C318 and HCFC-124 form azeotropic or azeotrope-like compositions comprising 26.8 mole% PFC-C318 and 73.2 mole% HCFC-124 at 0°C and 24.6 psia. From these data it has been calculated that PFC-C318 and HCFC-124 form azeotropic or azeotrope-like compositions comprising 27.5 mole% PFC-C318 and 72.5 mole% HCFC-124 forms at 80°C and 234.1 psia. Accordingly, the present invention further comprises an azeotropic or azeotrope-like composition comprising from 26.8 to 27.5 mole% PFC-C318 and from 73.2 to 72.5 mole% HCFC-124, said composition having a boiling point of from 0°C at 24.5 psia to 80°C at 234.1 psia.

Surprisingly, PFC-C318 and HFC-134 have been found by the present inventors to form an azeotropic composition comprising 25.0 mole% PFC-C318 and 75.0 mole% HFC-134 at 0°C and 36.4 psia. From these data it has been calculated that PFC-C318 and HFC-134 form azeotropic or azeotrope-like compositions comprising 24.6 mole% PFC-C318 and 75.4 mole% HFC-134 at -30.0° C and 10.35 psia. From these data it has been calculated that PFC-C318 and HFC-134 form azeotropic or azeotrope-like compositions comprising 23.2 mole% PFC-C318 and 76.8 mole% HFC-134 at 80°C and 325.8 psia. Accordingly, the present invention further comprises an azeotropic or azeotrope-like composition comprising from 24.6 to 23.2 mole% PFC-C318 and from 75.4 to 76.8 mole% HFC-134, said composition having a boiling point of from -30°C at 10.35 psia to 80°C at 325.8 psia.

Surprisingly, PFC-C318 and HFC-134a have been found by the present inventors to form an azeotropic composition comprising 7.4 mole% PFC-C318 and 92.6 mole% HFC-134a at 0°C and 43 psia. From these data it has been calculated that PFC-C318 and HFC-134a form azeotropic or azeotrope-like compositions comprising 9.9 mole% PFC-C318 and 90.1 mole% HFC-134a at -30°C and 12 psia. From these data it has been calculated that PFC-C318 and HFC-134a form azeotropic or azeotrope-like compositions comprising 0.6 mole% PFC-C318 and 99.4 mole% HFC-134a at 40°C and 147 psia. Accordingly, the present invention further comprises an azeotropic or azeotrope-like composition comprising from 9.9 to 0.6 mole% PFC-C318 and from 90.1 to 99.4 mole% HFC-134a, said composition having a boiling point of from -30°C at 12 psia to 40°C at 147 psia.

Surprisingly, PFC-C318 and HFC-152a have been found by the present inventors to form an azeotropic composition comprising 23.1 mole% PFC-C318 and 76.9 mole% HFC-152a at 0°C and 41 psia. From these data it has been calculated that PFC-C318 and HFC-152a form azeotropic or azeotrope-like compositions comprising 22.4 mole% PFC-C318 and 77.6 mole% HFC-152a at -20°C and 19 psia. From these data it has been calculated that PFC-C318 and HFC-152a form azeotropic or azeotrope-like compositions comprising 21.3 mole% PFC-C318 and 78.7 mole% HFC-152a at 80°C and 349 psia. Accordingly, the present invention further comprises an azeotropic or azeotrope-like composition comprising from 23.1 to 21.3 mole% PFC-C318 and from 76.9 to 78.7 mole% HFC-152a, said composition having a boiling point of from -20°C at 19 psia to 80°C at 349 psia.

In another aspect of the present invention, distilling mixtures comprising PFC-C318 and at least one of these halogenated impurities under conditions to form said low-boiling azeotropes comprising PFC-C318 and said impurity, and removing said azeotropic or azeotrope-like composition as the distillate product in a distillation, permits some degree of separation of PFC-C318 and said impurity. By azeotropic distillation is meant a process in which a distillation column is operated under conditions to cause an azeotropic or azeotrope-like composition to form, and the formation thereof changes the relative volatility of at least one component to another such that these components may be separated by distillation.

For example, a mixture comprising PFC-C318 and HCFC-124 can be partially purified by using the aforementioned azeotropic compositions. A distillation column can be operated at a pressure and temperature to cause a low-boiling azeotrope comprising PFC-C318 and HCFC-124 to form, and the

azeotrope can be removed as an overhead stream from the distillation column. If the concentration of PFC-C318 in the first mixture (the crude PFC-C318/HCF-124 mixture to be separated) is greater than that in an azeotrope of PFC-C318/HCF-124 formed under the distillation conditions, a PFC-C318 product
5 can be removed as a bottoms stream upon distillation of the first mixture wherein the HCF-124 concentration in the bottoms stream is reduced compared to the HCF-124 concentration in the first mixture, while the azeotropic PFC-C318/HCF-124 composition is removed as an overhead stream from the distillation column. Conversely, if the concentration of HCF-124 in the first
10 mixture is greater than that in an azeotropic composition comprising PFC-C318/HCF-124 formed under the distillation conditions, a HCF-124 product can be removed as a bottoms stream upon distillation of the first mixture with the PFC-C318 concentration in the bottoms stream reduced compared to the PFC-C318 concentration in the first mixture, while the azeotropic PFC-C318/HCF-124 composition is removed as an overhead stream from the distillation column.
15 Obtaining PFC-C318 with the concentration of HCF-124 in it reduced compared to a first PFC-C318/HCF-124 mixture (or obtaining HCF-124 with the concentration of PFC-C318 in it reduced compared to a first PFC-C318/HCF-124 mixture) in a single distillation would require starting with a composition
20 higher in PFC-C318 (or HCF-124) concentration than the azeotrope composition formed at that same temperature and pressure, but some portion of the PFC-C318 (or HCF-124) would necessarily remain as the PFC-C318/HCF-124 azeotrope.

Where formation and distillation of the respective PFC-C318 azeotropes (e.g., PFC-C318/HCF-124; PFC-C318/HFC-134; PFC-C318/HCF-124a; PFC-C318/HFC-134a; PFC-C318/HFC-152a) are employed for separating
25 PFC-C318 from halogenated impurities, the resultant azeotropic PFC-C318-containing compositions are useful as feed streams to a thermal process for manufacturing TFE and HFP. Alternately, the PFC-C318 in the distillate product may be separated substantially-free from halogenated impurities by the extractive
30 distillation process of the present invention.

However, although use of said azeotropic compositions in a distillation is useful for partial purification of the PFC-C318 or halogenated impurity, it is difficult to obtain high-recovery efficiency of substantially-pure PFC-C318 product from the starting PFC-C318/halogenated impurity mixture by
35 azeotropic distillation. Further, such azeotropic distillations most often do not provide for removal of other impurities that do not form azeotropic compositions with PFC-C318.

A number of the other halogenated impurities found in PFC-C318 manufacturing streams have relative volatilities that approach 1.0 relative to PFC-C318. Such halogenated impurities include CFC-12, HCC-20, HCFC-22, HFC-32, CFC-114, CFC-114a, CFC-217ba, HFC-227ea, PFC-1318my, PFC-1318c and FC-31-10. CFC-114, CFC-114a, PFC-1318my and FC31-10 are particularly problematic because they frequently appear in concentrations ranging from several hundred to several thousand parts-per-millions-molar or higher in PFC-C318 process streams. Separating these impurities from the PFC-C318 would require tall and expensive distillation columns, and it would still be extremely difficult if not impossible to obtain substantially-pure PFC-C318 in high-recovery efficiency from such mixtures.

The present inventors have found, unexpectedly, that PFC-C318 may be recovered substantially-free from these and other halogenated impurities by use of effective amounts of compounds that act in a non-ideal manner with at least one component of a PFC-C318/halogenated impurity first mixture. Such compounds, hereafter referred to as entraining-agents, increase or decrease the volatility of the PFC-C318 relative to at least one halogenated impurity in the first mixture under distillation conditions, thus allowing PFC-C318 that is substantially-free of halogenated impurity to be obtained from a first mixture comprising PFC-C318 and halogenated impurity.

Thus, the present invention further comprises processes for separating PFC-C318 from at least one halogenated impurity, said processes comprising extractive distillation of a mixture comprising PFC-C318 and halogenated impurity in the presence of at least one entraining agent. The process further comprises a distillation in which the volatility of PFC-C318 or halogenated impurity is increased, one relative to the other, in the presence of an entraining agent.

By entraining agent is meant any compound that, when added to a first mixture comprising PFC-C318 and halogenated impurity, interacts with at least one of PFC-C318 and halogenated impurity so as to change the volatility of one of these components relative to the other component in the mixture such that the PFC-C318 and halogenated impurity may be separated by distillation.

By effective amount of entraining agent is meant an amount of at least one entraining agent that, in the presence of PFC-C318 and halogenated impurity, causes the volatility of the halogenated impurity to increase or decrease relative to PFC-C318 sufficiently to allow separation by distillation of the halogenated impurity from the PFC-C318. This definition includes the case when the effective

amount may vary depending on the pressure applied to the composition so long as the change in relative volatility continues to exist.

By extractive distillation is meant a process in which an entraining agent is introduced at an upper feed point of a distillation column, whereas the mixture requiring separation is introduced at the same, or preferably a relatively lower feed point in the column than the point at which the entraining agent is introduced. The entraining agent passes down through trays or packing in the column and exits as a column bottoms stream with one or more components of the mixture to be separated. While in the presence of the entraining agent, at least one of the components to be separated becomes relatively either more or less volatile compared to at least one of the other components in the mixture, with that more volatile component exiting as a distillation column overhead stream. Entraining agents that are fed to a distillation column at a point equal to, or higher than, the mixture to be separated and that pass down through the column thus enabling a separation by distillation, are herein referred to as extractive distillation agents or extractants.

Further defining the present extractive distillation process, the present inventors have discovered that any one of the halogenated impurities FC-31-10, FC-1318my, FC-1318c, HFC-134, HFC-134a, HCFC-124, HCFC-124a, CFC-114, CFC-114a, CFC-217ba, HCC-20 and optionally other halogenated compounds that may be present in a PFC-C318-containing stream may be separated from said PFC-C318 by the use of entraining agents in an extractive distillation process. Suitable entraining agents that may be used as extractants for the separation of PFC-C318 from these halogenated impurities include: ethers, ketones, alcohols, hydrocarbons, and hydrochlorocarbons. Suitable entraining agents that may be used as extractants in the present invention preferably have normal boiling points of from 30 °C to 120 °C. Suitable ethers include tetrahydrofuran (THF), 1,4-dioxane and dialkyl ethers such as methyl tertiarybutyl ether (MTBE). Suitable ketones include acetone and methylethylketone (MEK). Suitable alcohols include methanol and propanol. Suitable hydrocarbons include toluene and cyclohexane. Suitable hydrochlorocarbons include chloroform (CHCl₃). The preferred entraining agents for separating halogenated impurities from PFC-C318 by extractive distillation are THF, MEK and 1,4-dioxane.

The relative volatility of said halogenated impurities compared to PFC-C318 in the absence of said extractants makes the halogenated impurity difficult to separate from the PFC-C318 by conventional distillation. In the presence of at least one said extractant, the volatility of PFC-C318 surprisingly changes compared to the aforementioned halogenated impurities. Thus, in the

presence of any one of the extractants, the PFC-C318 may be separated by extractive distillation from said halogenated impurities and obtained as a product substantially-free of said halogenated impurities. The present invention also provides a method of removing PFC-C318 from said halogenated impurities to
5 recover said halogenated impurities as a product stream substantially-free of PFC-C318.

With the exception of certain halogenated impurities such as FC-31-10, the halogenated impurities unexpectedly become less volatile than PFC-C318 in the presence of the extractants of the present invention. In the presence of the
10 extractants, PFC-C318 substantially-free of halogenated impurities may thus be obtained as an extractive distillation column overhead stream, and with the halogenated impurities recovered together with the extractant as a distillation column bottom stream.

Thus the present invention further comprises a process for separating
15 PFC-C318 and at least one of said halogenated impurities, comprising: a.) contacting a first mixture comprising PFC-C318 and at least one halogenated impurity with an entraining agent to form a second mixture, and b.) distilling the second mixture and recovering a distillation column overhead stream comprising PFC-C318 and a distillation column bottom stream comprising entraining agent
20 and at least one halogenated impurity.

In contrast to the other aforementioned halogenated impurities, PFC-31-10, which is normally higher boiling than PFC-C318, surprisingly becomes even more volatile than PFC-C318 in the presence of the present extractants such that the PFC-31-10 may be separated from the PFC-C318 as an extractive
25 distillation column overhead stream, with PFC-C318 substantially-free of PFC-31-10 obtained as an extractive distillation column bottom stream.

Thus the present invention further comprises a process for separating PFC-C318 and PFC-31-10, comprising: a.) contacting a first mixture comprising PFC-C318 and PFC-31-10 with an entraining agent to form a second mixture, and
30 b.) distilling the second mixture and recovering a distillation column overhead stream comprising PFC-31-10 and a distillation column bottom stream comprising entraining agent and PFC-C318.

Figure 1 schematically illustrates a system that can be used to perform aspects of the present extractive distillation process. A first mixture comprising
35 PFC-C318 and FC-31-10 is supplied via conduit 1 to distillation column 2. At least one extractive entraining agent, e.g. THF, is supplied via conduit 3 to distillation column 2 at a feed point higher in the column than the feed point of the mixture to be separated, e.g., PFC-C318 and FC-31-10. The overhead distillate

from the column is sent via conduit 4 to condenser 5. At least part of the condensed distillate stream is returned to the column 2 as reflux 6. The remainder of the condensed distillate is recovered via conduit 7 as FC-31-10 product substantially-free of PFC-C318 and THF. A stream comprising PFC-C318 and THF that is substantially-free of FC-31-10 is removed from the column 2 bottoms via conduit 8 and may be recovered as product. Alternately, the column bottoms stream 8 may be fed to distillation column 9, which is operated so as to strip compounds from the entraining agent. The distillate from column 9 is fed via conduit 10 to condenser 11. From condenser 11, some amount of condensed distillate is returned to the column 9 as reflux via conduit 12, while the remainder is recovered as product, e.g. as PFC-C318 substantially-free of FC-31-10 and extractive entraining agent, via conduit 13. Extractive entraining agent, e.g. THF, with the concentration of non-THF compounds reduced compared to their concentrations in stream 8 is obtained as the distillation column bottoms 14. Stream 14 may optionally be returned to distillation column 2 as extractant feed, fed to the column at a feed point higher in the column than that feed point of the mixture to be separated, e.g. FC-31-10 and PFC-C318, or may be optionally mixed with stream 3.

Figure 1 may also be used to schematically illustrate a system that can be used to perform another embodiment of the present inventive extractive distillation process. A first mixture comprising PFC-C318 and FC-1318my is supplied via conduit 1 to distillation column 2. At least one extractive entraining agent, e.g. THF, is supplied via conduit 3 to distillation column 2 at a feed point higher in the column than the feed point of the mixture to be separated, e.g., PFC-C318 and FC-1318my. The overhead distillate from the column is sent via conduit 4 to condenser 5. At least part of the condensed distillate stream is returned to the column 2 as reflux 6. The remainder of the condensed distillate is recovered via conduit 7 as PFC-C318 product substantially-free of FC-1318my and THF. A stream comprising FC-1318my and THF that is substantially-free of PFC-C318 is removed from the column 2 bottoms via conduit 8 and may be recovered as product. Alternately, the column bottoms stream 8 may be fed to distillation column 9, which is operated so as to strip compounds other than the entraining agent from the entraining agent. The distillate from column 9 is fed via conduit 10 to condenser 11. From condenser 11, some amount of condensed distillate is returned to the column 9 as reflux via conduit 12, while the remainder is recovered as product, e.g. as FC-1318my substantially-free of PFC-C318 and extractive entraining agent, via conduit 13. Extractive entraining agent, e.g. THF, with the concentration of non-THF compounds reduced compared to their

concentrations in stream 8, is obtained as the distillation column bottoms 14. Stream 14 may optionally be returned to distillation column 2 as extractant feed, fed to the column at a feed point higher in the column than that feed point of the mixture to be separated, e.g. PFC-C318 and FC-1318my, or may be optionally
5 mixed with stream 3.

In conventional, azeotropic or extractive distillations, the overhead or distillate stream exiting the column may be condensed using conventional reflux condensers. At least a portion of this condensed stream can be returned to the top of the column as reflux, and the remainder recovered either as product or for other
10 processing. The ratio of the condensed material that is returned to the top of the column as reflux to the material removed is commonly referred to as the reflux ratio. In those cases where an entraining agent is employed, the compounds and entraining agent exiting the column as bottoms stream can then be passed to a
15 stripper or other distillation column for separation by using conventional distillation or other known methods, and, if desired, for recycle of the entraining agent to the first distillation column.

The specific conditions that can be used for practicing the present processes depend upon a number of parameters, such as the diameter of the distillation column, feed points, number of separation stages in the column,
20 among others. The operating pressure of the distillation system may range from 15 to 500 psia, normally 50 to 400 psia. Typically, an increase in the extractant agent feed rate relative to the feed rate of the mixture to be separated causes an increase in the purity of the product to be recovered with regard to those component(s) being removed. Increasing the reflux ratio normally results in a decreased
25 extractant concentration in the distillate stream. But generally, the reflux ratio ranges between 1/1 to 200/1. The temperature of the condenser, that is located adjacent to the top of the column, is normally sufficient to substantially fully condense the distillate that is exiting from the top of the column, or is that temperature required to achieve the desired reflux ratio by partial condensation.

Mixtures comprising C-318 suitable for purification by the present
30 invention can be obtained from any manufacturing process or source that produces or generates a PFC-C318-containing mixture. PFC-C318 may, for example, be produced by pyrolysis of HCFC-22. Alternately, the PFC-C318-containing mixture can be obtained from any manufacturing process that uses PFC-C318 and
35 desires to recover said PFC-C318 from said process. If desired, conventional distillation can be used for reducing initial amounts of halogenated impurities. That is to say, conventional distillation can be used for removing relatively large or bulk quantities of halogenated impurities from the PFC-C318-containing

mixture that in turn may then be processed in accordance with the present inventive processes for recovering and purifying a PFC-C318.

EXAMPLES

5 The following examples are provided to illustrate aspects of the present inventive processes, and are not intended to limit the scope of the present invention. The following examples employ the NRTL interaction parameters identified earlier. In the following examples, each stage is based upon a 100% operational or performance efficiency. Differing column designs and operating
10 conditions are employed using different extractive agents in order to maximize the performance of each distillation. In all examples, the total stages include condenser and reboiler, with the condenser counted as stage No. 1. In all examples, stream flows are expressed in pounds-per-hour (pph) or in moles-per-hour (mph); temperatures ("TEMP") are expressed in degrees Celsius (°C);
15 concentrations are expressed in mole percent (mole%), weight percent (wt%), parts-per-million-molar (ppm-molar), and parts-per-million-by-weight (ppm-wt); heat flow rates ("DUTIES") removed from the condenser or put into the reboiler of the distillation columns are expressed in pcu/hour or pcu/hr; and pressures ("PRES") are expressed in pounds-per-square-inch-absolute (psia). Various
20 values are also shown for the distillation column bottoms ("BTMS"), distillate ("DIST"), condenser ("CONDSTR"), reflux ("REFLUX") and top ("TOP"). Values are also shown with regard to the stream fed to the column for separation ("FEED") and any extractant fed to the column ("EXTR" or "EXTR FEED"). In these Examples, by recovery efficiency ("RECOV. EFF.") is meant the percent of
25 the C318 fed to the distillation that is recovered in the C318 product stream

Comparative Examples 1,2,3

30 In Comparative Examples 1 through 3, a mixture comprising 980 pph PFC-C318 and 20 pph C₄F₁₀ (PFC-31-10) is fed to a distillation column, then distilled using conventional distillation under conditions such that a PFC-C318 product stream is removed from the column as distillate and a C₄F₁₀ product stream is removed as column bottoms. The specific conditions of and results from the distillations are shown in Table 1.

TABLE 1

COMPARATIVE			
EXAMPLE NUMBER	1	2	3
40 Extractant	NONE	NONE	NONE

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	# STAGES		114	228	144
	FEED STAGE		58	114	72
5	REFLUX TEMP	(°C)	7.3	7.3	7.3
	DIST TEMP	(°C)	7.3	7.3	7.3
	BTMS TEMP	(°C)	10.7	10.7	13.5
	FEED TEMP	(°C)	10.5	10.5	10.5
10	TOP PRES	(PSIA)	24.7	24.7	24.7
	CONDSR PRES	(PSIA)	24.7	24.7	24.7
	BTMS PRES	(PSIA)	27.7	27.7	24.7
15	DISTILLATE RATE	(PPH)	800.0	800.0	975.0
	REFLUX RATE	(PPH)	13888.0	28551.0	160531.0
	BOTTOMS RATE	(PPH)	200.0	200.0	25.0
	CONDENSER DUTY(PCU/HR)		-385645.	-770645.	-4240779.
	REBOILER DUTY (PCU/HR)		+385000.	+770000.	+4240000.
20	<u>FEED</u>				
	<u>FLOWS</u>				
	PFC-C318	(PPH)	980.	980.	980.
	C ₄ F ₁₀	(PPH)	20.	20.	20.
	<u>COMPOSITION</u>				
25	C ₄ F ₁₀	(PPM-WT)	20000.	20000.	20000.
	C ₄ F ₁₀	(PPM-MOLAR)	16861.	16861.	16861.
	<u>COLUMN DISTILLATE</u>				
	<u>FLOWS</u>				
30	PFC-C318	(PPH)	799.40	800.0	975.0
	C ₄ F ₁₀	(PPH)	0.60	0.00	0.0073
	<u>COMPOSITION</u>				
	C ₄ F ₁₀	(PPM-WT)	754.	4.1	7.5
	C ₄ F ₁₀	(PPM-MOLAR)	634.	3.4	6.3
35	PFC-C318 RECOV.EFF. (%)		81.57	81.63	99.49
	<u>COLUMN BOTTOMS</u>				
	<u>FLOWS</u>				
40	PFC-C318	(PPH)	180.6	180.0	5.0
	C ₄ F ₁₀	(PPH)	19.40	20.00	19.99

In Comparative Example 1, the PFC-C318 product stream from this conventional distillation contains 634 ppm C₄F₁₀ and the PFC-C318 recovery efficiency is only about 82%.

45 In Comparative Example 2, the number of column stages and the reboiler heat duty are both doubled compared to Comparative Example 1. In spite of this, the resulting PFC-C318 product still contains more than 3 ppm C₄F₁₀, and the PFC-C318 recovery efficiency is only about 82%.

50 In Comparative Example 3, the distillation is run with a reflux rate approximately ten times that of Comparative Example 1, and the PFC-C318 bottoms takeoff rate is reduced to approximately one tenth that of Comparative

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Example 1. Although the recovery efficiency increases to 99%, the PFC-C318 product stream still contains 6.3 ppm C_4F_{10} .

These Comparative Examples demonstrate the difficulty of obtaining by conventional distillation a substantially-pure PFC-C318 product stream with high-recovery efficiency from a first stream comprising PFC-C318 and C_4F_{10} .

Comparative Examples 4, 5

In Comparative Examples 4 and 5, a mixture comprising PFC-C318 and the impurities shown below in Table 2 is fed to a distillation column. The mixture is distilled using conventional distillation under conditions such that a product stream comprising PFC-C318 is removed from the column as distillate and a product stream comprising the impurities are removed as column bottoms. The specific conditions of and results from the distillations are shown in Table 2.

		<u>TABLE 2</u>	
		4	5
COMPARATIVE EXAMPLE NUMBER			
Extractant		NONE	NONE
# STAGES		114	228
FEED STAGE		58	114
TOP TEMP (°C)		7.3	7.3
REFLUX TEMP (°C)		7.3	7.3
DIST TEMP (°C)		7.3	7.3
BTMS TEMP (°C)		10.5	10.5
FEED TEMP (°C)		10.5	10.5
TOP PRES (PSIA)		24.7	24.7
CONDSR PRES (PSIA)		24.7	24.7
BTMS PRES (PSIA)		27.7	27.7
DISTILLATE RATE (PPH)		800.0	800.0
REFLUX RATE (PPH)		20360.	41118.
BOTTOMS RATE (PPH)		200.	200.
CONDENSER DUTY (PCU/HR)		-555645.	-1100645.
REBOILER DUTY (PCU/HR)		+555000.	+1100000.
<u>FEED</u>			
<u>FLOWS</u>			
PFC-C318 (PPH)		998.9	998.9
CFC-114 (PPH)		1.0	1.0
HFC-124a (PPH)		0.200E-01	0.200E-01
CFC-217ba (PPH)		0.10	0.10
PFC-1318my (PPH)		0.200E-01	0.200E-01
<u>COMPOSITION</u>			
TOT IMPURITIES (PPM-WT)		1140.0	1140.0
TOT IMPURITIES (PPM-MOLAR)		1317.2	1317.2
<u>COLUMN DISTILLATE</u>			

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	<u>FLOWS</u>		
	PFC-C318 (PPH)	799.9	800.0
	CFC-114 (PPH)	0.345E-01	0.440E-03
	HCFC-124a (PPH)	0.200E-01	0.200E-01
5	CFC-217ba (PPH)	0.552E-02	0.117E-03
	PFC-1318my (PPH)	0.139E-05	0.439E-10
	<u>COMPOSITION</u>		
	CFC-114 (PPM-MOLAR)	50.4	0.64
	HCFC-124a (PPM-MOLAR)	36.6	36.6
10	CFC-217ba (PPM-MOLAR)	6.7	0.14
	PFC-1318my (PPM-MOLAR)	0.0017	0.548E-07
	TOT IMPURITIES (PPM-MOLAR)	93.8	37.4
	PFC-C318 (WT %)	99.992503	99.997430
	PFC-C318 (MOLE %)	99.990620	99.996257
15	<u>PFC-C318 RECOV. EFF. (%)</u>	80.09	80.09

COLUMN BOTTOMS

	<u>FLOWS</u>		
	PFC-C318 (PPH)	198.9	198.9
20	CFC-114 (PPH)	0.97	1.00
	HCFC-124a (PPH)	0.105E-17	0.467E-33
	CFC-217ba (PPH)	0.09	0.10
	PFC-1318my (PPH)	0.200E-01	0.200E-01

25 Under the conditions of the distillation of Comparative Example 4, the PFC-C318 is recovered as distillate product with only 80% recovery efficiency and still containing 94 ppm total impurities.

In Comparative Example 5, the number of column stages and the reflux rate are both doubled compared to Comparative Example 4. In spite of this,
30 the PFC-C318 is recovered still with only 80% PFC-C318 recovery efficiency and still containing 37 ppm total impurities.

These Comparative Examples show the difficulty in using conventional distillation to produce a substantially-pure PFC-C318 product stream with high-recovery efficiency from a first stream comprising PFC-C318 and a
35 variety of impurities common to PFC-C318 process streams.

Comparative Example 6,7,8,9

In Comparative Examples 6, 7, 8 and 9 a stream comprising 394 pph PFC-C318 and 606 pph HFC-134 is fed to a distillation column. These are
40 distilled using the variety of conditions and with the results shown in Table 3.

TABLE 3

45	COMPARATIVE EXAMPLE NUMBER	6	7	8	9
	Extractant	NONE	NONE	NONE	NONE
	# STAGES	62	62	62	62
	Feed Stage	30	30	30	30

50

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	TOP TEMP	(C)	-10.1	-10.1	-10.1	-10.1
	REFLUX TEMP	(C)	-10.2	-10.2	-10.2	-10.2
	DIST TEMP	(C)	-10.2	-10.2	-10.2	-10.2
	BTMS TEMP	(C)	-7.3	-7.3	-7.3	-7.3
5	FEED TEMP	(C)	-7.3	-7.3	-7.3	-7.3
	TOP PRES	(PSIA)	24.7	24.7	24.7	24.7
	CONDSR PRES	(PSIA)	24.7	24.7	24.7	24.7
	BTMS PRES	(PSIA)	27.7	27.7	27.7	27.7
10	DISTILLATE RATE	(PPH)	100.0	900.0	100.0	900.0
	REFLUX RATE	(PPH)	2000.	2000.	20000.	20000.
	BOTTOMS RATE	(PPH)	900.	100.	900.	100.
15	CONDENSER DUTY (PCU/HR)		-89975.	-124251.	-861187.	-895463.
	REBOILER DUTY (PCU/HR)		+89896.	+123544.	+861108.	+894755.
	<u>FEED</u>					
	<u>FLows</u>					
20	PFC-C318	(PPH)	394.0	394.0	394.0	394.0
	HFC-134	(PPH)	606.0	606.0	606.0	606.0
	<u>COMPOSITION</u>					
	PFC-C318	(WT %)	39.4	39.4	39.4	39.4
	PFC-C318	(MOLE %)	24.9	24.9	24.9	24.9
25	<u>COLUMN DISTILLATE</u>					
	<u>FLows</u>					
	PFC-C318	(PPH)	39.4	354.7	39.4	354.7
	HFC-134	(PPH)	60.6	545.3	60.6	545.3
30	<u>COMPOSITION</u>					
	PFC-C318	(WT %)	39.4	39.4	39.4	39.4
	PFC-C318	(MOLE %)	24.9	24.9	24.9	24.9
	<u>COLUMN BOTTOMS</u>					
35	<u>FLows</u>					
	PFC-C318	(PPH)	354.6	39.3	354.6	39.3
	HFC-134	(PPH)	545.4	60.7	545.4	60.7
	<u>COMPOSITION</u>					
	PFC-C318	(WT %)	39.4	39.3	39.4	39.3
40	PFC-C318	(MOLE %)	24.9	24.9	24.9	24.9

As may be seen in these Comparative Examples, there is essentially no separation of the PFC-C318 from the HFC-134 as a result of this distillation, even over a wide range of distillate rates, bottoms rates and reflux rates. This is because the PFC-C318 and HFC-134 feed rates to this distillation column comprise the azeotrope composition formed by PFC-C318 and HFC-134 at the column operating conditions. This Comparative Example shows the futility of separating an azeotropic composition comprising PFC-C318 and HFC-134 by conventional distillation.

50

Comparative Examples 10,11,12,13

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In Comparative Examples 10, 11, 12 and 13 a mixture comprising PFC-C318 and HFC-134 is fed to a distillation column. The conditions of and results from these distillations are shown in Table 4.

5

TABLE 4

Comparative EXAMPLE NUMBER		10	11	12	13
10	Extractant	NONE	NONE	NONE	NONE
	#STAGES	32	32	32	32
	FEED STAGE	12	12	12	12
	TOP TEMP (°C)	1.4	-1.3	-10.0	-10.1
15	REFLUX TEMP (°C)	-5.6	-7.7	-10.2	-10.2
	DIST TEMP (°C)	-5.6	-7.7	-10.2	-10.2
	BTMS TEMP (°C)	10.5	10.5	10.5	10.5
	FEED TEMP (°C)	3.7	3.7	3.7	3.7
20	TOP PRES (PSIA)	24.8	24.8	24.8	24.8
	CONDSR PRES (PSIA)	24.7	24.7	24.7	24.7
	BTMS PRES (PSIA)	27.7	27.7	27.7	27.7
	DISTILLATE RATE (PPH)	338.8	226.5	86.7	82.5
25	REFLUX RATE (PPH)	150.	300.	400.	500.
	BOTTOMS RATE (PPH)	661.	774.	913.	917.
	CONDENSER DUTY (PCU/HR)	-15741.	-17960.	-20505.	-24961.
	REBOILER DUTY (PCU/HR)	+16067.	+18619.	+21747.	+26225.
30	<u>FEED</u>				
	<u>FLOWS</u>				
	PFC-C318 (PPH)	950.	950.	950.	950.
	HFC-134 (PPH)	50.	50.	50.	50.
35	<u>COMPOSITION</u>				
	HFC-134 (PPM-WT)	50000.	50000.	50000.	50000.
	HFC-134 (PPM-MOLAR)	93532.	93532.	93532.	93532.
	<u>DISTILLATE</u>				
40	<u>FLOWS</u>				
	PFC-C318 (PPH)	288.8	176.5	36.7	32.5
	HFC-134 (PPH)	50.0	50.0	50.0	50.0
	<u>COMPOSITION</u>				
	PFC-C318 (WT %)	85.2	77.9	42.3	39.4
45	PFC-C318 (MOLE %)	74.7	64.3	27.2	24.9
	<u>BOTTOMS</u>				
	<u>FLOWS</u>				
	PFC-C318 (PPH)	661.2	773.5	913.3	917.5
50	HFC-134 (PPH)	0.00003	0.00004	0.00005	0.00005
	<u>COMPOSITION</u>				
	HFC-134 (PPM-MOLAR)	0.1	0.1	0.1	0.1
	PFC-C318 (WT %)	99.99999	99.99999	99.99999	99.99999
	PFC-C318 (MOLE %)	99.99999	99.99999	99.99999	99.99999
55	PFC-C318 RECOV.EFF. (%)	69.6	81.4	96.1	96.6

In these examples, the distillation column is operated under conditions such that a PFC-C318/HFC-134 azeotrope composition is formed having a lower PFC-C318 concentration than that of the feed mixture. The low-boiling HFC-134/PFC-C318 azeotrope goes overhead in the column and PFC-C318 that was
 5 fed in excess of that azeotrope composition is recovered in the column bottoms stream.

As the reflux rate is increased between Comparative Examples 10, 11, 12 and 13, the efficiency of the distillation column in separating the excess PFC-C318 from the azeotropic composition increases, such that more of this excess
 10 may be recovered as an PFC-C318 substantially free of HFC-134 as column bottoms. However, this increased efficiency requires significant increases in reflux rates and significant decreases in distillate product rates to obtain. Further, some of the PFC-C318 fed necessarily remains in the distillate as part of the PFC-C318/HFC-134 azeotrope composition, limiting the PFC-C318 recovery
 15 efficiency possible from such an azeotropic distillation.

Nevertheless, these Comparative Examples show how low-boiling azeotropic compositions comprising PFC-C318 and HFC-134 may be used to remove HFC-134 from a first mixture comprising PFC-C318 and HFC-134 such that a PFC-C318 product stream substantially-free of HFC-134 may be obtained.
 20

Comparative Example 14, 15, 16, 17

In Comparative Examples 14, 15, 16 and 17, a mixture comprising PFC-C318 and HFC-134 is fed to a distillation column. The conditions of and
 25 results from these distillations are shown in Table 5.

TABLE 5

COMPARATIVE EXAMPLE NUMBER				
	14	15	16	17
Extractant	NONE	NONE	NONE	NONE
# STAGES	62	62	62	62
FEED STAGE	30	30	30	30
35 TOP TEMP (°C)	-8.3	-9.3	-10.1	-10.1
REFLUX TEMP (°C)	-9.1	-9.9	-10.2	-10.2
DIST TEMP (°C)	-9.1	-9.9	-10.2	-10.2
BTMS TEMP (°C)	-4.3	-4.3	-4.3	-4.3
40 FEED TEMP (°C)	-5.2	-5.2	-5.2	-5.2
TOP PRES (PSIA)	24.7	24.7	24.7	24.7
CONDSR PRES (PSIA)	24.7	24.7	24.7	24.7
BTMS PRES (PSIA)	27.7	27.7	27.7	27.7
45 DISTILLATE RATE (PPH)	389.2	206.9	126.9	126.9

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	REFLUX RATE (PPH)	500.	1000.	1500.	2000.
	BOTTOMS RATE (PPH)	611.	793.	873.	873.
	CONDENSER DUTY (PCU/HR)	-44097.	-56438.	-69704.	-91127.
5	REBOILER DUTY (PCU/HR)	+43827.	+56376.	69760.	91182.

FEEDFLOWS

	PFC-C318 (PPH)	50.	50.	50.	50.
10	HFC-134 (PPH)	950.	950.	950.	950.
	<u>COMPOSITION</u>				
	PFC-C318 (PPM-WT)	50000.	50000.	50000.	50000.
	PFC-C318 (PPM-MOLAR)	26144.	26144.	26144.	26144.

15 COLUMN DISTILLATEFLOWS

	PFC-C318 (PPH)	50.0	50.0	50.0	50.0
	HFC-134 (PPH)	339.2	156.9	76.9	76.9
	<u>COMPOSITION</u>				
20	PFC-C318 (WT %)	12.8	24.2	39.4	39.4
	PFC-C318 (MOLE %)	7.0	14.0	24.9	24.9

COLUMN BOTTOMSFLOWS

25	PFC-C318 (PPH)	0.00012	0.00016	0.00017	0.00017
	HFC-134 (PPH)	610.8	793.1	873.1	873.1
	<u>COMPOSITION</u>				
	PFC-C318 (PPM-MOLAR)	0.1	0.1	0.1	0.1
	HFC-134 (WT %)	99.99998	99.99998	99.99998	99.99998
30	HFC-134 (MOLE %)	99.99999	99.99999	99.99999	99.99999
	<u>HFC-134 RECOV. EFF. (%)</u>	64.3	83.5	91.9	91.9

In these examples, the distillation column is operated under distillate temperature conditions such that a PFC-C318/HFC-134 azeotrope composition is formed having a lower HFC-134 concentration than that of the feed mixture. The low-boiling HFC-134/PFC-C318 azeotrope goes overhead in the column and HFC-134 that was fed in excess of that azeotrope composition is recovered in the column bottoms stream.

As the reflux rate is increased and the distillate rate decreased between Comparative Examples 14, 15, 16 and 17, the efficiency of the distillation column in separating the excess HFC-134 increases, such that more of this excess may be recovered as an HFC-134 substantially-free of PFC-C318. However, this increased efficiency requires significant increases in reflux rates and decreases in distillate product rates increasing the energy expended for the distillation. Further, some of the HFC-134 fed necessarily remains in the distillate as part of the PC-C318/HFC-134 azeotrope composition, limiting the HFC-134 recovery efficiency possible from such an azeotropic distillation.

Nevertheless, these Comparative Examples show how the low-boiling azeotropic compositions comprising PFC-C318 and HFC-134 may be used to

remove PFC-C318 from a first mixture comprising PFC-C318 and HFC-134 such that a HFC-134 product stream that is substantially-free of PFC-C318 may be obtained.

5

Comparative Examples 18 and 19

In Comparative Examples 18 and 19, a feed stream comprising PFC-C318 and C_4F_{10} is fed to a distillation column operated under the conditions shown in Table 6. An extractant stream comprising perfluorohexane (C_6F_{14}) is fed into the column as an extractant stream at a point above that of the PFC-C318/ C_4F_{10} feed. The results of these distillations are shown in Table 6.

10

TABLE 6

COMPARATIVE				
15	EXAMPLE NUMBER		18	19
	Extractant		C ₆ F ₁₄	C ₆ F ₁₄
	#STAGES		92	92
	EXTR FEED STAGE		10	10
20	FEED STAGE		40	40
	TOP TEMP	(°C)	7.3	7.3
	REFLUX TEMP	(°C)	7.3	7.3
	DIST TEMP	(°C)	7.3	7.3
25	BTMS TEMP	(°C)	74.8	75.4
	EXTR FEED TEMP	(°C)	10.0	10.0
	FEED TEMP	(°C)	10.5	10.5
	TOP PRES	(PSIA)	24.7	24.7
30	CONDSR PRES	(PSIA)	24.7	24.7
	BTMS PRES	(PSIA)	27.7	27.7
	DISTILLATE RATE	(PPH)	25.0	250.0
	REFLUX RATE	(PPH)	3000.	3000.
35	BOTTOMS RATE	(PPH)	100975.	100750.
	EXTRACTANT RATE	(PPH)	100000.	100000.
	EXTRACTANT (LB-MOLES/HR)		295.8	295.8
	CONDENSER DUTY	(PCU/HR)	-79435.	-85343.
40	REBOILER DUTY	(PCU/HR)	+1730243.	+1746685.
	<u>FEED</u>			
	<u>FLOWS</u>			
	PFC-C318 (PPH)		980.	980.
45	C ₄ F ₁₀ (PPH)		20.	20.
	EXTR. (PPH)		0.	0.
	<u>COMPOSITION</u>			
	C ₄ F ₁₀ (PPM-WT)		20000.	20000.
	C ₄ F ₁₀ (PPM-MOLAR)		16861.	16861.
50	<u>EXTRACTION COLUMN DISTILLATE</u>			
	<u>FLOWS</u>			
	PFC-C318 (PPH)		25.00	249.97

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	C ₄ F ₁₀ (PPH)	0.00	0.03
	EXTR. (PPH)	0.00	0.00
	<u>COMPOSITION</u>		
	C ₄ F ₁₀ (PPM-MOLAR)	64.	104.
5	PFC-C318 (WT %)	99.99235	99.98764
	PFC-C318 (MOLE %)	99.99357	99.98961

EXTRACTION COLUMN BOTTOMS

	<u>FLOWS</u>		
10	PFC-C318 (PPH)	955.	730.
	C ₄ F ₁₀ (PPH)	20.00	19.97
	EXTR. (PPH)	100000.	100000.
	<u>COMPOSITION</u>		
	C ₄ F ₁₀ (PPM-MOLAR)	17293.	22471.
15	PFC-C318 (WT %)	97.94891	97.33745
	PFC-C318 (MOLE %)	98.27068	97.75294
	PFC-C318 RECOV. EFF. (%)	97.45	74.49

In Comparative Examples 18 and 19, the feed stream composition is identical to that of Comparative Examples 1, 2 and 3. Even with an extremely high extractant feed rate, extremely tall columns and extremely high reflux rates, the C₄F₁₀ concentration in the PFC-C318 product has been reduced down to only slightly less than 100 ppm. Comparative Examples 18 and 19 show that when used as an extractant, C₆F₁₄ offers no advantage over the conventional distillation shown in Comparative Examples 1, 2 and 3 for this separation. C₆F₁₄ is one example of the many compounds ineffective as an extractant for facilitating the separation of PFC-C318 and C₄F₁₀ by extractive distillation.

Examples 20 through 31

In each of Examples 20 through 31, a crude feed stream comprising HFC-C318 and C₄F₁₀ is fed to a distillation column and operated under the conditions shown in Table 7. The concentrations of HFC-C318 and C₄F₁₀ in the feed stream for each of Examples 20 through 31 are identical to those of Comparative Examples 1, 2, 3, 18 and 19.

In each of Examples 20 through 31, a different compound is fed to the column as an extractive agent. The distillation columns in these Examples are operated to remove C₄F₁₀ from the column as overhead distillate, while recovering a PFC-C318 product as column bottoms. The extractants for each Example and the results of the distillations are shown in Table 7.

TABLE 7

EXAMPLE NUMBER		20	21	22	23	24	25	26

45	EXTRACTANT	ACETONE	MEK	THF	1,4-DIOXANE	CHCl ₃	PROPANOL	METHANOL
	#STAGES	72	72	72	72	72	72	72

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	EXTR FEED STAGE	15	15	15	5	10	10	10
	FEED STAGE	30	30	35	20	20	20	20
	TOP TEMP (°C)	37.7	40.5	40.5	40.6	40.3	40.5	37.7
5	REFLUX TEMP (°C)	37.6	40.3	40.3	40.3	40.1	40.3	37.5
	DIST TEMP (°C)	37.6	40.3	40.3	40.3	40.1	40.3	37.5
	BTMS TEMP (°C)	53.2	88.9	74.3	70.2	76.0	99.1	65.2
	EXTR FEED TEMP (°C)	40.0	40.0	40.0	40.0	40.0	40.0	40.0
	FEED TEMP (°C)	38.1	38.1	38.1	38.1	38.1	38.1	38.1
10	TOP PRES (PSIA)	64.7	64.7	64.7	64.7	64.7	64.7	64.7
	CONDENSER PRES (PSIA)	64.7	64.7	64.7	64.7	64.7	64.7	64.7
	BTMS PRES (PSIA)	67.7	67.7	67.7	67.7	67.7	67.7	67.7
15	DISTILLATE RATE (PPH)	25.9	25.1	25.2	25.0	25.7	25.0	25.3
	REFLUX RATE (PPH)	3000.	3000.	3000.	3000.	3000.	3000.	3000.
	BOTTOMS RATE (PPH)	5034.	9761.	10344.	13361.	19118.	22239.	15679.
	EXTRACTANT RATE (PPH)	4060.	8786.	9369.	12386.	18144.	21264.	14704.
	EXTRACTANT (LB-MOLES/HR)	69.9	121.9	129.9	140.6	152.0	353.8	458.9
20	CONDENSER DUTY (PCU/HR)	-72400.	-61347.	-62079.	-61072.	-63803.	-61537.	-70007.
	REBOILER DUTY (PCU/HR)	+105352.	+312053.	+213459.	+245962.	+227529.	+1004089.	+316004.
	<u>FEED</u>							
25	<u>FLows</u>							
	PFC-C318 (PPH)	980.	980.	980.	980.	980.	980.	980.
	C ₄ F ₁₀ (PPH)	20.	20.	20.	20.	20.	20.	20.
	EXTR. (PPH)	0.	0.	0.	0.	0.	0.	0.
	<u>COMPOSITION</u>							
30	C ₄ F ₁₀ (PPM-WT)	20000.	20000.	20000.	20000.	20000.	20000.	20000.
	C ₄ F ₁₀ (PPM-MOLAR)	16861.	16861.	16861.	16861.	16861.	16861.	16861.
	<u>EXTRACTION COLUMN DISTILLATE</u>							
	PFC-C318 (PPH)	5.00	5.00	5.00	5.00	5.00	5.00	5.00
35	C ₄ F ₁₀ (PPH)	20.0	20.0	20.0	20.0	20.0	20.0	20.0
	EXTR. (PPH)	0.95	0.07	0.16	0.05	0.71	0.05	0.30
	<u>EXTRACTION COLUMN BOTTOMS</u>							
	PFC-C318 (PPH)	975.	975.	975.	975.	975.	975.	975.
40	C ₄ F ₁₀ (PPH)	0.00116	0.00116	0.00116	0.00116	0.00116	0.00116	0.00116
	EXTR. (PPH)	4059.	8786.	9369.	12386.	18143.	21264.	14704.
	<u>COMPOSITION</u> - (values exclude extractant)							
	C ₄ F ₁₀ (PPM-MOLAR)	1.0	1.0	1.0	1.0	1.0	1.0	1.0
	PFC-C318 (WT %)	99.99988	99.99988	99.99988	99.99988	99.99988	99.99988	99.99988
45	PFC-C318 (MOLE %)	99.99990	99.99990	99.99990	99.99990	99.99990	99.99990	99.99990
	PFC-C318 RECOV.EFF. (%)	99.49	99.49	99.49	99.49	99.49	99.49	99.49

TABLE 7 (CONTINUED)

50	-----EXAMPLE NUMBER-----					
		27	28	29	30	31

	EXTRACTANT	MTBE	CYANE	TOLUENE	DEE	HEXANE
	NO. THEORETICAL STAGES	92	92	92	92	92
55	EXTR FEED STAGE	15	5	5	5	5
	FEED STAGE	35	25	25	35	35
	TOP TEMPERATURE (°C)	10.5	10.6	10.5	8.9	10.7

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	REFLUX TEMPERATURE	(°C)	10.3	10.3	10.3	8.8	10.4
	DIST TEMPERATURE	(°C)	10.3	10.3	10.3	8.8	10.4
	BTMS TEMPERATURE	(°C)	63.2	52.1	51.4	47.5	85.1
	EXTR FEED TEMP	(°C)	10.0	10.0	10.0	10.0	10.0
5	FEED TEMP	(°C)	10.5	10.5	10.5	10.5	10.5
	TOP PRESSURE	(PSIA)	24.7	24.7	24.7	24.7	24.7
	CONDSR PRESSURE	(PSIA)	24.7	24.7	24.7	24.7	24.7
	BTMS PRESSURE	(PSIA)	27.7	27.7	27.7	27.7	27.7
10							
	DISTILLATE RATE	(PPH)	25.1	25.0	25.0	26.5	25.2
	REFLUX RATE	(PPH)	3000.	3000.	3000.	3000.	3000.
	BOTTOMS RATE	(PPH)	20359.	19668.	24543.	29256.	60205.
	EXTRACTANT RATE	(PPH)	19385.	18694.	23568.	28283.	59231.
15	EXTRACTANT	(LB-MOLES/HR)	219.9	222.1	255.8	381.6	687.4
	CONDENSER DUTY	(PCU/HR)	-69856.	-69242.	-68832.	-81060.	-70072.
	REBOILER DUTY	(PCU/HR)	+619018.	+430629.	+479421.	+696617.	+2617593.
20	<u>PFC-C318/C₄F₁₀ FEED</u>						
	PFC-C318	(PPH)	980.	980.	980.	980.	980.
	C ₄ F ₁₀	(PPH)	20.	20.	20.	20.	20.
	EXTR.	(PPH)	0.	0.	0.	0.	0.
	<u>COMPOSITION</u>						
25	C ₄ F ₁₀	(PPM-WT)	20000.	20000.	20000.	20000.	20000.
	C ₄ F ₁₀	(PPM-MOLAR)	16861.	16861.	16861.	16861.	16861.
	<u>EXTRACTION COLUMN DISTILLATE</u>						
	<u>FLOWS</u>						
30	PFC-C318	(PPH)	5.00	5.00	5.00	5.00	5.00
	C ₄ F ₁₀	(PPH)	20.0	20.0	20.0	20.0	20.0
	EXTR.	(PPH)	0.15	0.05	0.00	1.48	0.16
	<u>EXTRACTION COLUMN BOTTOMS</u>						
	<u>FLOWS</u>						
35	PFC-C318	(PPH)	975.	975.	975.	975.	975.
	C ₄ F ₁₀	(PPH)	0.00116	0.00116	0.00116	0.00116	0.00116
	EXTR.	(PPH)	19384.	18693.	23568.	28281.	59230.
	<u>COMPOSITION - (values exclude extractant)</u>						
40	C ₄ F ₁₀	(PPM-MOLAR)	1.0	1.0	1.0	1.0	1.0
	PFC-C318	(WT %)	99.99988	99.99988	99.99988	99.99988	99.99988
	PFC-C318	(MOLE %)	99.99990	99.99990	99.99990	99.99990	99.99990
	PFC-C318 RECOV. EFF. (%)		99.49	99.49	99.49	99.49	99.49

45 By contrasting these Examples to Comparative Examples 1,2, 3 and to Comparative Examples 18 and 19, it may be seen that the extractive agents of Comparative Examples 20 through 33 significantly increase the effectiveness of the distillation for this separation, and are thus effective extractants for separating C₄F₁₀ from PFC-C318. In Examples 20 through 31, PFC-C318 having

50 significantly reduced concentrations of C₄F₁₀ versus the crude feed stream are recovered in the PFC-C318 product from the distillation column bottoms. Whereas concentrations of C₄F₁₀ in the PFC-C318 product below 10 ppm were extremely difficult or impossible to obtain in the Comparative Examples,

concentrations of C_4F_{10} of 1 ppm in the PFC-C318 product are obtained in each of the Examples in Table 7 with high-recovery efficiency of the PFC-C318 product.

The eleven extractants are shown in the order from most effective to least effective for the PFC-C318/ C_4F_{10} separation, with those more effective defined by those requiring lower molar flow rate of extractant required to produce PFC-C318 product containing 1 ppm C_4F_{10} . On this basis, the ranking of extractants from "most" to "least" effective is: acetone, methylethylketone (MEK), tetrahydrofuran (THF), 1,4-dioxane, chloroform ($CHCl_3$), methanol, methyl tertiarybutyl ether (MTBE), cyclohexane (CYANE), toluene, diethyl ether (DEE) and n-hexane. All of these extractants reverse the normal relative volatility of PFC-C318 and C_4F_{10} compared to a conventional distillation as in Comparative Examples 1,2 and 3, such that in the presence of the extraction solvent the C_4F_{10} is recovered in the distillate stream, while the PFC-C318 is recovered as the extractive distillation column bottoms. The extractive agents indicated in each of Examples 20 through 33 exiting with the PFC-C318 from the column bottoms may optionally be separated from the PFC-C318 by distillation or other methods.

While acetone is among the most effective extractants for the PFC-C318/ C_4F_{10} separation, acetone forms a low-boiling azeotrope with PFC-C318. While MEK, THF and 1,4-dioxane are all just about equally effective in separating PFC-C318 and C_4F_{10} , MEK and 1,4-dioxane form two liquid phases with PFC-C318 in the extraction column which requires more extractant flow and adds to the difficulty of operating the column. The extractants most preferred for this separation are consequently THF, followed by MEK and 1,4-dioxane.

Example 32

In this Example, a stream comprising PFC-C318 and C_4F_{10} is fed to an extractive distillation column, where THF is fed to the column as extractant at a point above that of the PFC-C318/ C_4F_{10} feed. The bottoms stream from the extraction column, comprising PFC-C318 and THF extractant, is then fed to a stripping column. In the stripping column, a PFC-C318 substantially-free of both C_4F_{10} and the THF extractant is obtained as distillate product, while the THF extractant is recovered as bottoms product, then recycled back to the extraction column as extractant feed. The operating conditions and results from these distillations are shown in Table 8.

TABLE 8

-----EXTRACTION COLUMN

STRIPPING COLUMN

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=====				=====			
	# STAGES	72		# STAGES	42		
	EXTR FEED STAGE	15		FEED STAGE	35		
	FEED STAGE	35					
5	TOP TEMP (°C)	40.5		TOP TEMP (°C)	7.4		
	REFLUX TEMP (°C)	40.3		REFLUX TEMP (°C)	7.3		
	DIST TEMP (°C)	40.3		DIST TEMP (°C)	7.3		
	BTMS TEMP (°C)	74.3		BTMS TEMP (°C)	85.6		
10	EXTR FEED TEMP (°C)	40.0		FEED TEMP (°C)	74.3		
	FEED TEMP (°C)	38.1					
	TOP PRES (PSIA)	64.7		TOP PRES (PSIA)	24.7		
	CONDSR PRES (PSIA)	64.7		CONDSR PRES (PSIA)	24.7		
15	BTMS PRES (PSIA)	67.7		BTMS PRES (PSIA)	26.7		
	DISTILLATE RATE (PPH)	25.2		DISTILLATE RATE (PPH)	975.0		
	REFLUX RATE (PPH)	3000.		REFLUX RATE (PPH)	4282.		
	BOTTOMS RATE (PPH)	10344.		BOTTOMS RATE (PPH)	9369.		
20	EXTRACTANT RATE (PPH)	9369.					
	EXTRACTANT (LB-MOLES/HR)	129.9					
	<u>FEED TO EXTRACTION COLUMN</u>			<u>FEED TO STRIPPING COLUMN</u>			
	<u>FLOWS</u>			<u>FLOWS</u>			
25	PFC-C318 (PPH)	980.		PFC-C318 (PPH)	975.		
	C ₄ F ₁₀ (PPH)	20.		C ₄ F ₁₀ (PPH)	0.0117		
	EXTR. (PPH)	0.		EXTR. (PPH)	9368.		
	<u>COMPOSITION</u>			<u>COMPOSITION</u>			
	C ₄ F ₁₀ (PPM-WT)	20000.					
30	C ₄ F ₁₀ (PPM-MOLAR)	16861.					
	<u>EXTRACTION COLUMN DISTILLATE</u>			<u>STRIPPING COLUMN DISTILLATE</u>			
	<u>FLOWS</u>			<u>FLOWS</u>			
	PFC-C318 (PPH)	5.00		PFC-C318 (PPH)	975.		
35	C ₄ F ₁₀ (PPH)	20.0		C ₄ F ₁₀ (PPH)	0.117E-02		
	EXTR. (PPH)	0.16		EXTR. (PPH)	0.176E-04		
	<u>COMPOSITION</u>			<u>COMPOSITION</u>			
	PFC-C318 (MOLE%)			PFC-C318 (MOLE%)	99.99989		
	C ₄ F ₁₀ (PPM-MOLAR)			C ₄ F ₁₀ (PPM-MOLAR)	1.0		
40	EXTR. (PPM-MOLAR)			EXTR. (PPM-MOLAR)	0.05		
	PFC-C318 RECOV. EFF. (%)			PFC-C318 RECOV. EFF. (%)	99.49		
	<u>EXTRACTION COLUMN BOTTOMS</u>			<u>STRIPPING COLUMN BOTTOMS</u>			
	<u>FLOWS</u>			<u>FLOWS</u>			
45	PFC-C318 (PPH)	975.		PFC-C318 (PPH)	0.5		
	C ₄ F ₁₀ (PPH)	0.00117		C ₄ F ₁₀ (PPH)	0.676E-08		
	EXTR. (PPH)	9368.		EXTR. (PPH)	9368.		

This example shows how the extractive distillation of the present invention may be used to produce a PFC-318 product substantially-free of both C₄F₁₀ and the THF extractant, with high-recovery efficiency of the PFC-C318. Starting from a feed stream comprising 980 pph PFC-C318 and 20 pph C₄F₁₀, a PFC-C318 product is obtained comprised of 1.0 ppm C₄F₁₀ and 0.05 ppm THF, with 99.5 recovery efficiency of the PFC-C318.

Example 33

Table 9 shows both the extractive distillation and stripping steps for purifying a crude PFC-C318 feed containing halogenated impurities comprising CFC-114, HCFC-124a, CFC-217ba and PFC-1318my. The extractant used is THF. The PFC-C318 product is recovered as extraction column distillate substantially-free of both the halogenated impurities and THF. The halogenated impurities are recovered in the extraction column bottoms stream along with the THF, this bottoms stream then sent as feed to a stripping column. The stripping column removes the organic impurities from the THF, the organic impurities recovered as the stripping column distillate, with the THF recovered as stripping column bottoms then recycled back to the extraction column as extractant feed.

TABLE 9

EXTRACTION COLUMN				STRIPPING COLUMN			
=====				=====			
	#STAGES		72		#STAGES		42
20	EXTR FEED STAGE		40		FEED STAGE		25
	FEED STAGE		55				
	TOP TEMP	(°C)	7.4		TOP TEMPERATURE	(°C)	11.3
	REFLUX TEMP	(°C)	7.3		REFLUX TEMPERATURE	(°C)	8.6
25	DIST TEMP	(°C)	7.3		DIST. TEMPERATURE	(°C)	8.6
	BTMS TEMP	(°C)	86.3		BTMS TEMPERATURE	(°C)	85.6
	EXTR FEED TEMP	(°C)	5.0		FEED TEMPERATURE	(°C)	87.2
	FEED TEMP	(°C)	10.5				
30	TOP PRES	(PSIA)	24.7		TOP PRESSURE	(PSIA)	24.7
	CONDSR PRES	(PSIA)	24.7		CONDSR PRESSURE	(PSIA)	24.7
	BTMS PRES	(PSIA)	27.7		BTMS PRESSURE	(PSIA)	26.7
	DISTILLATE RATE	(PPH)	993.9		DISTILLATE RATE	(PPH)	6.2
35	REFLUX RATE	(PPH)	5000.		REFLUX RATE	(PPH)	4274.
	BOTTOMS RATE	(PPH)	7995.		BOTTOMS RATE	(PPH)	7989.
	EXTRACTANT RATE	(PPH)	7989.				
	EXTRACTANT (LB-MOLES/HR)		110.8				
40	<u>EXTRACTION COLUMN FEED</u>				<u>STRIPPING COLUMN FEED</u>		
	<u>FLOWS</u>				<u>FLOWS</u>		
	PFC-C318	(PPH)	998.9		PFC-C318	(PPH)	5.0
	CFC-114	(PPH)	1.0		CFC-114	(PPH)	1.0
	HCFC-124a	(PPH)	0.200E-01		HCFC-124a	(PPH)	0.220E-01
45	CFC-217ba	(PPH)	0.10		CFC-217ba	(PPH)	0.10
	PFC-1318my	(PPH)	0.200E-01		PFC-1318my	(PPH)	0.200E-01
	EXTR.	(PPH)	0.0		EXTR.	(PPH)	7989.0
	<u>COMPOSITION</u>						
	TOT IMP (PPM-WT)		1140.0				
50	TOT IMP (PPM-MOLAR)		1317.2				

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EXTRACTION COLUMN DISTILLATE			STRIPPING COLUMN DISTILLATE		
<u>FLOWS</u>			<u>FLOWS</u>		
	PFC-C318 (PPH)	993.9		PFC-C318 (PPH)	5.0
	EXTR. (PPH)	0.678E-06		EXTR. (PPH)	0.10
5	<u>COMPOSITION</u>			CFC-114 (PPH)	1.0
	CFC-114 (PPM-MOLAR)	0.694E-02		HCFC-124a (PPH)	0.200E-01
	HCFC-124a (PPM-MOLAR)	0.202E-01		CFC-217ba (PPH)	0.990E-01
	CFC-217ba (PPM-MOLAR)	0.966E+00		PFC-1318my (PPH)	0.200E-01
	PFC-1318my (PPM-MOLAR)	0.496E-02			
10	EXTR. (PPM-MOLAR)	0.189E-02			
	TOT IMP (PPM-MOLAR)	0.100E+01			
	PFC-C318 (WT %)	99.999899			
	PFC-C318 (MOLE %)	99.999900			
	PFC-C318 RECOV. EFF. (%)	99.50			
15	<u>EXTRACTION COLUMN BOTTOMS</u>			<u>STRIPPING COLUMN BOTTOMS</u>	
	<u>FLOWS</u>			<u>FLOWS</u>	
	PFC-C318 (PPH)	5.0		PFC-C318 (PPH)	0.385E-17
	CFC-114 (PPH)	1.0		CFC-114 (PPH)	0.185E-03
20	HCFC-124a (PPH)	0.220E-01		HCFC-124a (PPH)	0.200E-02
	CFC-217ba (PPH)	0.10		CFC-217ba (PPH)	0.190E-14
	PFC-1318my (PPH)	0.200E-01		PFC-1318my (PPH)	0.924E-15
	EXTR. (PPH)	7989.		EXTR. (PPH)	7989.

Examples 34 - 40

Table 10 shows seven examples of different extraction solvents for removing PFC-C318 from HFC-134 to make substantially-pure HFC-134. The seven extractants are shown in the order from most effective to least effective for the PFC-C318/HFC-134 separation, with those more effective defined by those requiring lower molar flow rate of extractant required to produce 0.1 ppm PFC-C318 in the HFC-134 bottoms product. On this basis, the order from "most" to "least" effective is: 1,4-dioxane, tetrahydrofuran (THF), methyl ethyl ketone (MEK), methyl tertiarybutyl ether (MTBE), methanol, toluene, and propanol. In the presence of the extraction solvent the PFC-C318 is recovered in the distillate stream as a PFC-C318 product substantially-free of both HFC-134 and extractant, while the HFC-134 is recovered as the extractive distillation column bottoms along with the extractant. The extractive agent indicated may then optionally be separated from the HFC-134 by distillation or other methods.

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TABLE 10

EXAMPLE NUMBER	34	35	36	37	38	39	40
EXTRACTANT	1,4-Dioxane	THF	MEK	MTBE	METHANOL	TOLUENE	PROPANOL
#STAGES	62	62	62	62	62	62	62
45	EXTR FEED STAGE	8	8	8	8	8	8
	FEED STAGE	20	20	25	20	20	20
	TOP TEMP (°C)	7.4	7.4	7.4	7.5	6.5	7.4
	REFLUX TEMP (°C)	7.3	7.3	7.3	7.3	6.5	7.3
50	DIST TEMP (°C)	7.3	7.3	7.3	7.3	6.5	7.3

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	BTMS TEMP	(°C)	30.3	31.1	43.1	29.0	10.0	17.7	21.8
	EXTR FEED TEMP	(°C)	5.0	5.0	5.0	5.0	5.0	5.0	5.0
	FEED TEMP	(°C)	-5.2	-5.2	-5.2	-5.2	-5.2	-5.2	-5.2
5	TOP PRES	(PSIA)	24.7	24.7	24.7	24.7	24.7	24.7	24.7
	CONDSR PRES	(PSIA)	24.7	24.7	24.7	24.7	24.7	24.7	24.7
	BTMS PRES	(PSIA)	27.7	27.7	27.7	27.7	27.7	27.7	27.7
	DISTILLATE RATE	(PPH)	50.0	50.0	50.0	50.2	50.3	50.0	50.0
10	REFLUX RATE	(PPH)	300.	300.	300.	300.	300.	300.	300.
	BOTTOMS RATE	(PPH)	2245.	2156.	2382.	2780.	1748.	3540.	4776.
	EXTRACTANT RATE	(PPH)	1295.	1206.	1432.	1830.	798.	2590.	3826.
	EXTRACTANT	(LB-MOLES/HR)	14.7	16.7	19.9	20.8	24.9	28.1	63.7
15	<u>FEED</u>								
	<u>FLows</u>								
	PFC-C318	(PPH)	50.	50.	50.	50.	50.	50.	50.
	HFC-134	(PPH)	950.	950.	950.	950.	950.	950.	950.
	EXTR.	(PPH)	0.	0.	0.	0.	0.	0.	0.
20	<u>COMPOSITION</u>								
	PFC-C318	(PPM-WT)	50000.	50000.	50000.	50000.	50000.	50000.	50000.
	PFC-C318	(PPM-MOLAR)	26144.	26144.	26144.	26144.	26144.	26144.	26144.
	<u>EXTRACTION COLUMN DISTILLATE</u>								
25	PFC-C318	(PPH)	50.00	50.00	50.00	50.00	50.00	50.00	50.00
	HFC-134	(PPH)	0.01	0.01	0.01	0.01	0.01	0.01	0.01
	EXTR.	(PPH)	0.124E-4	0.346E-1	0.293E-1	0.143	0.307	0.159E-3	0.544E-8
	<u>EXTRACTION COLUMN BOTTOMS</u>								
30	<u>FLows</u>								
	PFC-C318	(PPH)	0.00019	0.00019	0.00019	0.00019	0.00019	0.00019	0.00019
	HFC-134	(PPH)	950.	950.	950.	950.	950.	950.	950.
	EXTR.	(PPH)	1295.	1206.	1432.	1830.	798.	2590.	3826.
	<u>COMPOSITION</u> - (values exclude extractant)								
35	PFC-C318	(PPM-MOLAR)	0.1	0.1	0.1	0.1	0.1	0.1	0.1
	HFC-134	(WT %)	99.99998	99.99998	99.99998	99.99998	99.99998	99.99998	99.99998
	HFC-134	(MOLE %)	99.99999	99.99999	99.99999	99.99999	99.99999	99.99999	99.99999
	<u>HFC-134 RECOV. EFF.</u>	(%)	100.00	100.00	100.00	100.00	100.00	100.00	100.00

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Examples 41, 42

Table 11 shows both the operating conditions and results for Examples 41 and 42. These Examples show an extractive distillation with THF as the extractant in which PFC-C318 and HFC-134, respectively, are recovered from a feed mixture comprising 60.6 wt% HFC-134 (75.1 mole %) and 39.4 wt% PFC-C318 (24.9 mole %). This feed composition comprises the azeotropic composition formed by HFC-134 and PFC-C318 at the temperatures of these distillation. As was shown in Comparative Examples 6, 7, 8 and 9, it is virtually impossible to separate said azeotropic composition of HFC-134 and PFC-C318 by conventional distillation.

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Examples 41 and 42, however, show extractive distillation using THF as the extractant enables the separation. In Example 41, the PFC-C318 product

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recovered as distillation column distillate contains 0.1 ppm total impurities (HFC-134 plus THF), and the recovery of PFC-C318 product is more than 99% of the PFC-C318 in the feed to the column. In Example 42, the HFC-134 product contains 0.1 ppm PFC-C318, and the recovery of HFC-134 product is essentially 100% of the HFC-134 in the feed to the column.

TABLE 11

EXAMPLE NUMBER	41	42
EXTRACTANT	THF	THF
#STAGES	62	62
EXTR FEED STAGE	40	15
FEED STAGE	50	30
TOP TEMP (°C)	7.4	7.4
REFLUX TEMP (°C)	7.3	7.3
DIST TEMP (°C)	7.3	7.3
BTMS TEMP (°C)	49.4	31.4
EXTR FEED TEMP (°C)	5.0	5.0
PFC-C318 FEED TEMP (°C)	-7.3	-7.3
TOP PRES (PSIA)	24.7	24.7
CONDSTR PRES (PSIA)	24.7	24.7
BTMS PRES (PSIA)	27.7	27.7
DISTILLATE RATE (PPH)	392.0	394.2
REFLUX RATE (PPH)	1231.	600.
BOTTOMS RATE (PPH)	2191.	1385.
EXTRACTANT RATE (PPH)	1583.	779.
EXTRACTANT (LB-MOLES/HR)	22.0	10.8
CONDENSER DUTY (PCU/HR)	-42621.	-26149.
REBOILER DUTY (PCU/HR)	83981.	43128.
<u>FEED</u>		
<u>FLOWS</u>		
PFC-C318 (PPH)	394.0	394.0
HFC-134 (PPH)	606.0	606.0
<u>COMPOSITION</u>		
HFC-134 (PPM-WT)	606000.0	606000.0
HFC-134 (PPM-MOLAR)	750956.6	750956.6
<u>EXTRACTION COLUMN DISTILLATE</u>		
<u>FLOWS</u>		
PFC-C318 (PPH)	392.0	394.0
HFC-134 (PPH)	0.999E-05	0.01
EXTR. (PPH)	0.706E-05	0.177
<u>COMPOSITION</u>		
HFC-134 (PPM-MOLAR)	0.05	49.7
EXTR. (PPM-MOLAR)	0.05	1250
TOT IMP (PPM-MOLAR)	0.10	1300
PFC-C318 (WT %)	99.999996	99.95
PFC-C318 (MOLE %)	99.999990	99.87
PFC-C318 RECOV. EFF. (%)	99.49	100.00

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EXTRACTION COLUMN BOTTOMS

<u>FLOWS</u>			
	PFC-C318 (PPH)	2.0	0.0
5	HFC-134 (PPH)	606.0	606.0
	EXTR. (PPH)	1583.	779.
<u>COMPOSITION</u> - (values exclude extractant)			
	PFC-C318 (PPM-MOLAR)	1680	0.10
	HFC-134 (WT %)	99.67	99.99998
10	HFC-134 (MOLE %)	99.83	99.99999
	<u>HFC-134 RECOV. EFF. (%)</u>	100.00	100.00

Examples 43, 44

In Examples 43 and 44, a stream comprising PFC-C318 and C₄F₁₀ is fed to an extractive distillation column, where THF is fed to the column as extractant at a point above that of the PFC-C318/C₄F₁₀ feed. The operating conditions and results from these distillations are shown in Table 12.

TABLE 12

20	EXAMPLE NUMBER		43	44

	Extractant		THF	THF
25	#STAGES		72	72
	EXTR FD STAGE		15	15
	PFC-C318 FD STAGE		35	35
	TOP TEMP	(°C)	40.5	40.5
30	REFLUX TEMP	(°C)	40.3	40.3
	DIST TEMP	(°C)	40.3	40.3
	BTMS TEMP	(°C)	74.3	82.7
	EXTR FEED TEMP	(°C)	40.0	40.0
	FEED TEMP	(°C)	38.1	38.1
35	TOP PRES	(PSIA)	64.7	64.7
	COND SR PRES	(PSIA)	64.7	64.7
	BTMS PRESSURE	(PSIA)	67.7	67.7
40	DISTILLATE RATE	(PPH)	25.2	25.2
	REFLUX RATE	(PPH)	3000.	3000.
	BOTTOMS RATE	(PPH)	10344.	13742.
	EXTRACTANT RATE	(PPH)	9369.	12767.
	EXTRACTANT	(LB-MOLES/HR)	129.9	177.1
45	CONDENSER DUTY	(PCU/HR)	-62079.	-62089.
	REBOILER DUTY	(PCU/HR)	+213459.	+316903.

FEED

50	<u>FLOWS</u>		
	PFC-C318 (PPH)	980.	980.
	C ₄ F ₁₀ (PPH)	20.	20.
	EXTR. (PPH)	0.	0.
<u>COMPOSITION</u>			
55	C ₄ F ₁₀ (PPM-WT)	20000.	20000.

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	C_4F_{10} (PPM-MOLAR)	16861.	16861.
	<u>EXTRACTION COLUMN DISTILLATE</u>		
	<u>FLOWS</u>		
5	PFC-C318 (PPH)	5.00	5.00
	C_4F_{10} (PPH)	20.0	20.0
	EXTR. (PPH)	0.16	0.16
	<u>EXTRACTION COLUMN BOTTOMS</u>		
10	<u>FLOWS</u>		
	PFC-C318 (PPH)	975.	975.
	C_4F_{10} (PPH)	0.00116	0.00116
	EXTR. (PPH)	9369.	12767.
	<u>COMPOSITION</u> - (values exclude extractant)		
15	C_4F_{10} (PPM-MOLAR)	1.0	0.1
	PFC-C318 (WT %)	99.99988	99.99999
	PFC-C318 (MOLE %)	99.99990	99.99999
	<u>PFC-C318 RECOV. EFF. (%)</u>	99.49	99.49

- 20 Example 43 is the same as the previous Example 22, and produces a PFC-C318 product as the extraction column bottoms stream comprising PFC-C318 containing 1.0 ppm C_4F_{10} with a PFC-C318 recovery efficiency of 99.5%. In Example 44, the extractant flow to the column is increased compared to that of Example 43, and produces a PFC-C318 product as extraction column bottoms
- 25 stream comprising PFC-C318 containing 0.1 ppm C_4F_{10} with a 99.5% PFC-C318 recovery efficiency.

EXAMPLE 45

This Example demonstrates the existence of azeotropic or azeotrope-like compositions between the binary pairs mixtures consisting essentially of

30 PFC-C318 and HCFC-124; PFC-C318 and HCFC-124a; PFC-C318 and HFC-134; PFC-C318 and HFC-134a; and PFC-C318 and HFC-152a. To determine the relative volatility of each binary pair, the PTx Method was used. In this procedure, for each binary pair, the total absolute pressure in a sample cell of

35 known volume was measured at constant temperature for various known binary compositions. These measurements were then reduced to equilibrium vapor and liquid compositions using the NRTL equation.

The vapor pressure measured versus the composition in the PTx cell for these binary systems are shown in Figures 3 through 7, respectively. The

40 experimental data points are shown in each Figure as solid points and the solid line is drawn from data calculated using the NRTL equation.

Referring now to Figure 2, Figure 2 illustrates graphically the formation of an azeotropic and azeotrope-like composition consisting essentially of PFC-C318 and HCFC-124 at 20°C, as indicated by a mixture of 26.9 mole %

PFC-C318 and 73.1 mole % HCFC-124 having the highest pressure over the range of compositions at this temperature. Based upon these findings, it has been calculated that an azeotropic or azeotrope-like composition of 26.9 mole% PFC-C318 and 73.1 mole% HCFC-124 is formed at 0°C and 24 psia, and an azeotropic or azeotrope-like composition of 27.5 mole% PFC-C318 and 72.5 mole% HCFC-124 is formed at 80°C and 234 psia. Accordingly, the present invention provides an azeotropic or azeotrope-like composition consisting essentially of from 26.9 to 27.5 mole% PFC-C318 and from 73.1 to 72.5 mole% HCFC-124, said composition having a boiling point of from 0°C at 24 psia to 80°C at 234 psia.

Referring now to Figure 3, Figure 3 illustrates graphically the formation of an azeotropic and azeotrope-like composition consisting essentially of PFC-C318 and HCFC-124a at 20°C, as indicated by a mixture of 22.4 mole % PFC-C318 and 67.6 mole % HCFC-124a having the highest pressure over the range of compositions at this temperature. Based upon these findings, it has been calculated that azeotropic or azeotrope-like compositions of 33.1 mole % PFC-C318 and 66.9 mole % HCFC-124a is formed at 0°C and 24 psia, and an azeotropic or azeotrope-like composition of 33.9 mole % PFC-C318 and 66.1 mole % HCFC-124a is formed at 80°C and 229 psia. Accordingly, the present invention provides an azeotropic or azeotrope-like composition consisting essentially of from 33.1 to 33.9 mole% PFC-C318 and from 66.9 to 66.1 mole% HCFC-124a, said composition having a boiling point of from 0°C at 24 psia to 80°C at 229 psia.

Referring now to Figure 4, Figure 4 illustrates graphically the formation of an azeotropic and azeotrope-like composition consisting essentially of PFC-C318 and HFC-134 at 0°C, as indicated by a mixture of 25.0 mole% PFC-C318 and 75.0 mole% HFC-134 having the highest pressure over the range of compositions at this temperature. Based upon these findings, it has been calculated that an azeotropic or azeotrope-like composition of 24.6 mole% PFC-C318 and 75.4 mole% HFC-134 is formed at -30°C and 10 psia, and an azeotropic or azeotrope-like composition of 23.2 mole% PFC-C318 and 76.8 mole% HFC-134 is formed at 80°C and 326 psia. Accordingly, the present invention provides an azeotropic or azeotrope-like composition consisting essentially of from 24.6 to 23.2 mole% PFC-C318 and from 75.4 to 76.8 mole% HFC-134, said composition having a boiling point of from -30°C at 10 psia to 80°C at 326 psia.

Referring now to Figure 5, Figure 5 illustrates graphically the formation of an azeotropic and azeotrope-like composition consisting essentially of PFC-C318 and HFC-134a at 0°C, as indicated by a mixture of 7.4 mole% PFC-C318 and 92.6 mole % HFC-134a having the highest pressure over the range of

compositions at this temperature. Based upon these findings, it has been calculated that an azeotropic or azeotrope-like compositions of 9.9 mole% PFC-C318 and 90.1 mole% HFC-134a is formed at -30°C and 12 psia, and an azeotropic or azeotrope-like composition of 0.6 mole% PFC-C318 and 99.4 mole% HFC-134a is formed at 40°C and 147 psia. Accordingly, the present invention provides an azeotropic or azeotrope-like composition consisting essentially of from 9.9 to 0.6 mole% PFC-C318 and from 90.1 to 99.4 mole % HFC-134a, said composition having a boiling point of from -30°C at 12 psia to 40°C at about 147 psia.

Referring now to Figure 6, Figure 6 illustrates graphically the formation of an azeotropic and azeotrope-like composition consisting essentially of PFC-C318 and HFC-152a at 0°C, as indicated by a mixture of 23.1 mole% PFC-C318 and 76.9 mole% HFC-152a having the highest pressure over the range of compositions at this temperature. Based upon these findings, it has been calculated that azeotropic or azeotrope-like compositions of 22.4 mole% PFC-C318 and 77.6 mole% HFC-152a is formed at -20°C and 19 psia, and an azeotropic or azeotrope-like composition of 21.3 mole% PFC-C318 and 78.7 mole% HFC-152a is formed at 80°C and 234 psia. Accordingly, the present invention provides an azeotropic or azeotrope-like composition consisting essentially of from 23.1 to 21.3 mole% PFC-C318 and from 76.9 to 78.7 mole% HFC-152a, said composition having a boiling point of from -20°C at 19 psia to 80 °C at 349 psia.

WHAT IS CLAIMED IS:

1.) A process for separating perfluorocyclobutane (PFC-C318) from halogenated impurity, comprising:

5 distilling a mixture of perfluorocyclobutane (PFC-C318) and halogenated impurity in the presence of an entraining agent selected from the group consisting of ethers, ketones, alcohols, saturated hydrocarbons and saturated hydrochlorocarbons, and

10 recovering perfluorocyclobutane (PFC-C318) containing less than 10 parts-per-million-molar of halogenated impurity.

2.) The process of claim 1 wherein perfluorocyclobutane (PFC-C318) is recovered as a distillation column overhead stream, and entraining agent and halogenated impurity are recovered as a distillation column bottom stream.

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3.) The process of claim 1 wherein halogenated impurity is recovered as a distillation column overhead stream and entraining agent and perfluorocyclobutane (PFC-C318) are recovered as a distillation column bottom stream.

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4.) The process of claim 1 wherein said mixture comprising perfluorocyclobutane (PFC-C318) and halogenated impurity is an azeotropic or azeotrope-like composition.

25

5.) The process of claim 4 wherein said azeotropic or azeotrope-like composition consists essentially of from 26.8 to 27.5 mole percent of perfluorocyclobutane (PFC-C318) and from 73.1 to 72.5 mole percent of 2-chloro-1,1,1,2-tetrafluoroethane (HCFC-124), said composition having a boiling point of from 0°C at 24 psia to 80°C at 234 psia.

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6.) The process of claim 4 wherein said azeotropic or azeotrope-like composition consists essentially of from 24.6 to 23.2 mole percent of perfluorocyclobutane (PFC-C318) and from 75.4 to 76.8 mole percent of 1,1,2,2-tetrafluoroethane (HFC-134), said composition having a boiling point of from -30 °C at 10 psia to 80°C at 326 psia.

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7.) The process of claim 4 wherein said azeotropic or azeotrope-like

composition consists essentially of from 9.9 to 0.6 mole percent of perfluorocyclobutane (PFC-C318) and from 90.1 to 99.4 mole percent of 1,1,1,2-tetrafluoroethane (HFC-134a), said composition having a boiling point of from -30°C at 12 psia to 40°C at 147 psia.

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8.) The process of claim 4 wherein said azeotropic or azeotrope-like composition consists essentially of from 23.1 to 21.3 mole percent of perfluorocyclobutane (PFC-C318) and from 76.9 to 78.7 mole percent of 1,1-difluoroethane (HFC-152a), said composition having a boiling point of from -20°

10 C at 19 psia to 80°C at 349 psia.

9.) The process of claim 1 wherein the halogenated impurity comprises at least one of PFC-31-10 (C_4F_{10}), PFC-41-12 (C_5F_{12}), PFC-1318my (cis- and trans- $CF_3CF=CFCF_3$), PFC-1318c ($CF_3CF_2CF=CF_2$), PFC-1216 ($CF_3CF=CF_2$), PFC-1114 ($CF_2=CF_2$) perfluoroisobutene ($CF_2=C(CF_3)_2$), CFC-114 (CF_2ClCF_2Cl), CFC-114a ($CFCl_2CF_3$), CFC-216ba ($CF_3CFCICF_2Cl$), CFC-217ba ($CF_3CCIFCF_3$), CFC-1113 ($CCIF=CF_2$), HCFC-124 ($CHFCICF_3$), HCFC-124a ($CCIF_2CHF_2$), HFC-134 (CHF_2CHF_2), HFC-134a (CH_2FCF_3), HFC-152a (CH_3CF_2H), HFC-125 (CF_3CF_2H), HFC-227ca ($CF_3CF_2CHF_2$), HFC-227ea (CF_3CHFCF_3), HFC-1225zc ($CF_3CH=CF_2$), HFC-236ca ($CHF_2CF_2CHF_2$), HFC-236ea (CHF_2CHFCF_3), HFC-236fa ($CF_3CH_2CF_3$), HCC-30 (CH_2Cl_2), HCC-40 (CH_3Cl) and HCC-160 (CH_3CH_2Cl).

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10.) The process of claims 1-9 wherein the ethers are selected from the group consisting of methyl tertiarybutyl ether, tetrahydrofuran and 1,4-dioxane; the ketones are selected from the group consisting of propanone (acetone) and 2-butanone (methyl ethyl ketone); the alcohols are selected from the group consisting of methanol and propanol; the hydrocarbon is cyclohexane; and the hydrochlorocarbon is chloroform.

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11.) The process of claims 1-9 wherein said perfluorocyclobutane (PFC-C318) is recovered containing less than 1 parts-per-million-molar of halogenated impurity.

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12.) The process of claims 1-9 wherein perfluorocyclobutane (PFC-C318) is recovered containing less than 100 parts-per-billion-molar of halogenated impurity.

- 13.) A process for separating perfluorocyclobutane (PFC-C318) from a first mixture of perfluorocyclobutane (PFC-C318) and halogenated impurity selected from the group consisting of 1,1,2,2-tetrafluoroethane (HFC-134), 1,1,1,2-tetrafluoroethane (HFC-134a) or 1,1-difluoroethane (HFC-152a), wherein
5 the amount of perfluorocyclobutane (PFC-C318) in the first mixture is in excess of the amount of perfluorocyclobutane (PFC-C318) in an azeotropic or azeotrope-like composition of perfluorocyclobutane (PFC-C318) and halogenated impurity, comprising:
- a.) distilling the first mixture to form an azeotropic or azeotrope-like
10 composition of perfluorocyclobutane (PFC-C318) and halogenated impurity as a second mixture, wherein said azeotropic or azeotrope-like composition is selected from the group consisting of:
- i.) an azeotropic or azeotrope-like composition consisting essentially of from 24.6 to 23.2 mole percent of perfluorocyclobutane
15 (PFC-C318) and from 75.4 to 76.8 mole percent of 1,1,2,2-tetrafluoroethane (HFC-134), said composition having a boiling point of from -30°C at 10 psia to 80°C at 326 psia,
- ii.) an azeotropic or azeotrope-like composition consisting essentially of from 9.9 to 0.6 mole percent of perfluorocyclobutane (PFC-
20 C318) and from 90.1 to 99.4 mole percent of 1,1,1,2-tetrafluoroethane (HFC-134a), said composition having a boiling point of from -30°C at 12 psia to 40°C at 147 psia, or
- iii.) an azeotropic or azeotrope-like composition consisting essentially of from 23.1 to 21.3 mole percent of perfluorocyclobutane
25 (PFC-C318) and from 76.9 to 78.7 mole percent of 1,1-difluoroethane (HFC-152a), said composition having a boiling point of from -20°C at 19 psia to 80°C at 349 psia, and
- b.) recovering said azeotropic or azeotrope-like composition as a distillation column overhead stream and perfluorocyclobutane (PFC-C318) as a
30 distillation column bottom stream.

- 14.) A process for separating perfluorocyclobutane (PFC-C318) from a first mixture of perfluorocyclobutane (PFC-C318) and halogenated impurity selected from the group consisting of 1,1,2,2-tetrafluoroethane (HFC-134),
35 1,1,1,2-tetrafluoroethane (HFC-134a) or 1,1-difluoroethane (HFC-152a), wherein the amount of halogenated impurity in the first mixture is in excess of the amount of halogenated impurity in an azeotropic or azeotrope-like composition of perfluorocyclobutane (PFC-C318) and halogenated impurity, comprising:

a.) distilling the first mixture to form an azeotropic or azeotrope-like composition of perfluorocyclobutane (PFC-C318) and halogenated impurity as a second mixture, wherein said azeotropic or azeotrope-like composition is selected from the group consisting of:

- 5 i.) an azeotropic or azeotrope-like composition consisting essentially of from 24.6 to 23.2 mole percent of perfluorocyclobutane (PFC-C318) and from 75.4 to 76.8 mole percent of 1,1,2,2-tetrafluoroethane (HFC-134), said composition having a boiling point of from -30°C at 10 psia to 80°C at 326 psia,
- 10 ii.) an azeotropic or azeotrope-like composition consisting essentially of from 9.9 to 0.6 mole percent of perfluorocyclobutane (PFC-C318) and from 90.1 to 99.4 mole percent of 1,1,1,2-tetrafluoroethane (HFC-134a), said composition having a boiling point of from -30°C at 12 psia to 40°C at 147 psia, or
- 15 iii.) an azeotropic or azeotrope-like composition consisting essentially of from 23.1 to 21.3 mole percent of perfluorocyclobutane (PFC-C318) and from 76.9 to 78.7 mole percent of 1,1-difluoroethane (HFC-152a), said composition having a boiling point of from -20°C at 19 psia to 80°C at 349 psia, and
- 20 b.) recovering said azeotropic or azeotrope-like composition as a distillation column overhead stream and halogenated impurity as a distillation column bottom stream.